

# THE CHEMISTRY OF RUBBER BY

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## PREFACE

FROM the time of the discovery of vulcanisation until comparatively recently the manufacture of rubber goods was conducted on an almost entirely empirical basis, and very few attempts were made to elucidate the nature of the processes involved in the production of vulcanised rubber.

During the past ten or twenty years, however, mainly as a result of researches on the chemical and physical characteristics of rubber, improved methods of manufacture have been evolved and new light thrown on old-established practices.

Apart from the manufacturing side of the industry, the development of plantation rubber, which became an important factor in the supply of raw material as recently as 1910, has necessitated the carrying out of a considerable amount of research work of a chemical nature.

The importance of chemistry in the rubber industry can, therefore, no longer be doubted, and in writing this book the aim has been to deal as fully as possible with the chemical principles involved in the cultivation, the collection, and manufacture of rubber. At the same time consideration has been given to the concomitant changes in physical properties accompanying the process of vulcanisation.

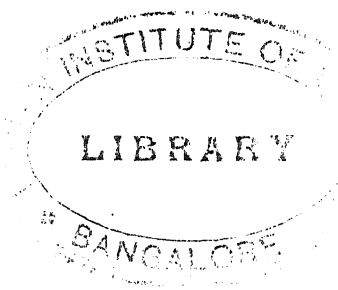
The synthesis of rubber has not been discussed at great length, but the space allotted is, in the author's opinion, commensurate with the technical importance of the subject at the present day.

No attempt has been made to describe in detail plantation practice, as there are numerous treatises devoted to this branch of the subject; only so much has been included as may be necessary for a proper appreciation of the terms which must be employed in the context.

The author wishes to express his thanks to the Rubber Growers' Association (Inc.) for the loan of photographs illustrating methods of preparing plantation rubber, and to The North British Rubber Company, Ltd., for supplying photographs of plant and for permitting the inclusion of numerous experimental data obtained in their laboratories.

B. D. W. L.

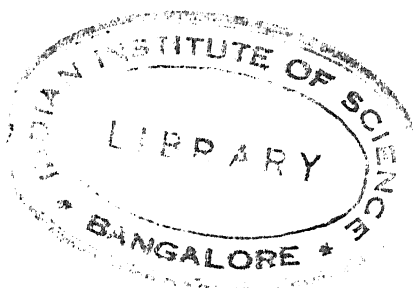




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# INSTITUTE OF LITERATURE BANKING TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES

<i>Analyst</i> . . . . .	The Analyst.
<i>Annalen</i> . . . . .	Liebig's Annalen der Chemie.
<i>Ann. Chim. Phys.</i> . . . .	Annalen de chimie et de physique (now issued as two separate journals).
<i>Ann. Rept. Appl. Chem.</i> . .	Annual Reports of Applied Chemistry issued by the Society of Chemical Industry.
<i>Agric. Bull. F.M.S.</i> . . .	Agricultural Bulletin of the Federated Malay States.
<i>Archief</i> . . . . .	Archief voor de Rubbercultuur in Nederlandsch-Indië.
<i>Arch. Pharm.</i> . . . . .	Archiv der Pharmazie.
<i>Ber.</i> . . . . .	Berichte der Deutschen Chemischen Gesellschaft.
<i>Bull. Imp. Inst.</i> . . . . .	Bulletin of the Imperial Institute.
<i>Bull. R. G. A.</i> . . . . .	Bulletin of the Rubber Growers' Association.
<i>Bull. Soc. Chim.</i> . . . . .	Bulletin de la société chimique de France.
<i>Bull. No. 27 F.M.S.</i> . . . .	Department of Agriculture, Federated Malay States, Bulletin No. 27, The Preparation and Vulcanisation of Plantation Para Rubber, by B. J. Eaton, J. Grantham, and F. W. F. Day.
<i>Chem. and Met. Eng.</i> . . . .	Chemical and Metallurgical Engineering.
<i>Chem. News</i> . . . . .	Chemical News.
<i>Chem. Soc. Abs.</i> . . . . .	Journal of the Chemical Society; Abstracts.
<i>Chem. Soc. Proc.</i> . . . . .	Proceedings of the Chemical Society, London.
<i>C. T. J.</i> . . . . .	Chemical Trade Journal.
<i>Chem. Weekblad</i> . . . . .	Chemisch Weekblad.
<i>Chem. Zeit.</i> . . . . .	Chemiker Zeitung.
<i>Chem. Zentr.</i> . . . . .	Chemisches Zentralblatt.
<i>Comm. Cent. Rubber-station</i>	Communication of the Central Rubber-station, Buitenzorg; reprinted from the Archief.
<i>Compt. rend.</i> . . . . .	Comptes rendus de l'Academie des Sciences.
<i>Delft Comm.</i> . . . . .	Communications of the Netherland Government Institute for advising the Rubber Trade and the Rubber Industry established at Delft. English Edition.
<i>Gazz. Chim. Ital.</i> . . . . .	Gazetta Chimica Italiana.
<i>Goodyear</i> . . . . .	Gum Elastic, and its Varieties, with a detailed account of its applications and uses, and of the discovery of Vulcanisation. Vols. I and II. 1855, New Haven.
<i>Gummi Zeit.</i> . . . . .	Gummi Zeitung (Berlin).
<i>Hancock</i> . . . . .	Personal Narrative of the Origin and Progress of the Caoutchouc or India Rubber Manufacture in England, by Thomas Hancock, 1857. Republished by James Lyne Hancock, Limited, London, 1920.
<i>Helv. Chim. Acta</i> . . . . .	Helvetica Chimica Acta.

## TABLE OF ABBREVIATIONS

<i>I. R. J.</i> . . . . .	India Rubber Journal (London).
<i>I. R. W.</i> . . . . .	India Rubber World (New York).
<i>Int. Cong. Appl. Chem.</i> . . . . .	International Congress of Applied Chemistry.
<i>J. Amer. Chem. Soc.</i> . . . . .	Journal of the American Chemical Society.
<i>J. Amer. Soc. Testing Materials</i> . . . . .	Journal of the American Society for Testing Materials.
<i>Jour. Franklin Inst.</i> . . . . .	Journal of the Franklin Institute.
<i>J. I. E. C.</i> . . . . .	Journal of Industrial and Engineering Chemistry.
<i>Jour. Pharm. Chim.</i> . . . . .	Journal de Pharmacie et de Chimie.
<i>J. prakt. Chem.</i> . . . . .	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . . . .	Journal of the Physical-Chemical Society of Russia.
<i>J. S. C. I.</i> . . . . .	Journal of the Society of Chemical Industry.
<i>Kroll. Chem. Beihefte</i> . . . . .	Kolloidchemische Beihefte.
<i>Koll. Zeit.</i> . . . . .	Kolloid Zeitschrift (formerly Zeitschrift für Chemie und Industrie der Kolloide).
<i>Le Caout. et la G. P.</i> . . . . .	Le Caoutchouc et la Gutta Percha (Paris).
<i>Phil. Trans.</i> . . . . .	Philosophical Transactions of the Royal Society of London.
<i>Quart. Jour. Sci.</i> . . . . .	Quarterly Journal of Science.
<i>Rec. Trav. Chim.</i> . . . . .	Recueil des Travaux chimiques des Pays-Bas.
<i>Rubber Age</i> . . . . .	Rubber Age (London).
<i>Rubber Industry</i> . . . . .	The Rubber Industry. Official Report of the International Congress of the Rubber Industry, 1911, 1914.
<i>Trans. Chem. Soc.</i> . . . . .	Transactions of the Chemical Society (London).
<i>Z. angew. Chem.</i> . . . . .	Zeitschrift für angewandte Chemie.
<i>Z. anorg. Chem.</i> . . . . .	Zeitschrift für anorganische und allgemeine Chemie.

# THE CHEMISTRY OF RUBBER

## CHAPTER I

### INTRODUCTORY AND HISTORICAL

RUBBER, INDIA-RUBBER, or CAOUTCHOUC\* is the name given to the elastic substance prepared from the milky fluid, or "latex," secreted by certain plants occurring chiefly in tropical regions.

Long before specimens were seen in Europe, travellers in the Indies and in Mexico had reported how the natives were in the habit of playing games with balls made from an elastic gum obtained from a tree.†

Little further was known of this material until 1736, when Charles-Marie de la Condamine, a French scientist, forwarded to the Académie des Sciences samples of a "blackish resinous mass" which he had collected in the forests on the slopes of the Andes in Ecuador. La Condamine set out from La Rochelle in 1735 as a member of an expedition sent by the King of France to the Equator for the purpose of measuring an arc of the meridian. Landing at a port before the remainder of the party, he proceeded to reach Quito, where he ultimately rejoined his colleagues, by a route which led him through little-known territory. In the course of his journey he had carefully noted the flora of the country, and in spite of hardships had preserved specimens, among which were the ones which he forwarded to the French Academy. "In the province of Esmeralda," wrote La Condamine, "there grows a tree called by the natives 'Hévé,' from which, by making an incision, there exudes a milky liquid which gradually hardens and darkens in the air, and in this condition is used by the natives for making torches." In the province of Quito this "resin" was said to be used for coating cloth, which would serve for the same purpose as waxed cloths. "The same tree grows by the banks of the Amazon, and the Indians give the name 'cahutchu' to the resin, from which they make boots which will resist water and which in appearance closely resemble real leather. Bottles

\* The term caoutchouc is now usually employed to denote the purified hydrocarbon constituent; rubber is taken to mean the raw material as it occurs in nature.

† Ovideo y Valdez, *Historia general y natural de las Indias*, Seville, 1535; Antonia de Herrera, *Historia general de los Castellanos en las islas y tierra firme de Mar Oceana*, Madrid, 1601.

are also made by drying the juice on earthen moulds and subsequently breaking up the earth and discharging it from the bottle neck." \* From the native name "cahutchu" was derived the name "caoutchouc," which was adopted both in this country and in France.

This elastic body was found in French Guiana in 1751 by Fresneau, who regarded it as "a kind of condensed resinous oil." It was subsequently discovered in Malaya in 1798 by James Howison, a surgeon resident in Penang, although it may be noted that the plant from which it was obtained belongs to an entirely different botanical order from that which was afterwards introduced on the plantation.

La Condamine himself quickly adapted his discovery to practical use, and prepared coated fabrics which served to protect the delicate instruments belonging to the expedition from the torrential rains frequently encountered.

Little use appears to have been made of the substance in Europe for some time, although Magalhaens had proposed its employment for rubbing out pencil-marks, and Joseph Priestley, the famous English chemist, who drew attention to this property, is generally credited with having suggested the name "Indian-Rubber." †

As at this period the latex could not be transported long distances without "coagulation" or clotting taking place, it is evident that the utilisation of india-rubber at all extensively was possible only to the natives, who were able to work with latex freshly drawn from the tree. In this way it was possible to make articles by dipping into the fluid suitable clay moulds and drying the adherent latex over a fire so that the mould became covered with a layer of india-rubber; the proofing of cloth was similarly a relatively simple matter. Only the solid material, however, could reach Europe, and hence many attempts were made to restore to the india-rubber its original fluidity so that the native practices could be imitated. It was soon evident that the substance possessed properties which distinguished it from ordinary "resins"; for example, Macquer and Herissant showed that whereas spirit of wine would dissolve ordinary resins, caoutchouc was not so affected. They found, however, that a solution could be obtained by immersing in oil of turpentine, and later Macquer discovered that ether was equally efficacious; at the same time it was noted that these solutions were not milky, like the natural liquid, but were quite clear and transparent, although not possessing the same fluidity.

These discoveries do not appear to have been put to any industrial use

\* *Histoire de l'Académie des Sciences*, 1751, p. 314.

† Later the prefix was dropped and the simple name "Rubber" was adopted. Cf. Hancock, p. vii. In the preface to Priestley's *Introduction to the Theory of Perspective*, 1770, there is a note to the effect that he had seen "a substance excellently adapted to the purpose of wiping from paper the marks of a black lead pencil." The word Indian-Rubber, however, was not mentioned.

until 1791, when Samuel Peal \* patented a method of rendering waterproof "all kinds of leather, cotton, linen, and woollen cloths, silks, stuffs, paper, wood, and other manufactures and substances, for the purpose of being worked up into shoes, boots, and other wearing apparel, and to be used on all occasions where dryness or a power of repelling wet or moisture may be required." The method consisted in applying to the material a coating of caoutchouc dissolved in oil of turpentine or other spirit; alternatively the gum in the native fluid state could be employed.

Although oil of turpentine was capable of dissolving caoutchouc, the solution thus obtained would not dry readily on account of the comparatively high boiling point of the solvent, and little progress was made in the proofing of cloth until help came from a quite unexpected direction.

The time when these early experiments were being made synchronised with the introduction of coal-gas for the purpose of lighting the dwellings and streets of cities. The makers of this gas began to find considerable quantities of ammonia liquor and tar accumulate, and were anxious to find an outlet for these by-products.

In the case of the Glasgow gas works the proprietors in 1819 entered into a contract with Charles Macintosh, who agreed to purchase the whole of their by-products, as he intended to employ the ammonia in the manufacture of cudbear. For the "coal oil" or naphtha no useful application could be found until Macintosh discovered that it would dissolve india-rubber, and in 1823 he took out a patent for a process of waterproofing textiles with the aid of such a solution. The rubber coating was covered with a second textile layer, and the combination or "double-texture" fabric became known as Macintosh, a name which persists to this day.

At about the period when coal-tar naphtha became available as a solvent, Thomas Hancock in London was working assiduously on the fashioning of useful articles from rubber, his attention being at first directed to the making of elastic attachments for clothing, as, for example, for the wristbands of gloves, for hose tops, or for the sides of boots, to obviate the use of laces. These articles were cut from rubber prepared by the natives and sent to this country in the form of sheets or bottles. Hancock extended his investigations to the proofing of fabrics, entering into an arrangement with Macintosh, who had established a factory at Manchester for the same purpose. So quickly did the business develop that by 1830 such articles as air-cushions, beds, pillows, life-belts were being made in large quantities. Thus the results achieved in the rubber-growing countries by the natives, who, by using the fresh latex,

\* E.P. No. 1801, 1791.



were able to render fabrics waterproof, were capable of being reproduced in this country by dissolving the dried rubber in coal-tar naphtha and coating the fabrics with this solution.

Hancock's attention was not confined entirely to the preparation and employment of rubber solutions as proofing agents, but the possibilities of using the latex itself were also considered, as in 1824 small supplies came forward in good condition.\* In 1830 he appointed an agent in Tampico to collect and forward consignments, which were despatched in well-sealed barrels; in the majority of cases, however, coagulation had taken place during transit, and after some little time the project of importing latex was abandoned. It was found later that the addition of ammonia prevented coagulation,† but although several small lots arrived without mishap, the application of the latex for proofing purposes was not developed further.

In the course of his experiments Hancock sought for some means of preparing sheets of solid rubber; although he was able to produce very thin sheets by evaporating a solution, they were not suitable for making articles of any description. It is true that he could utilise pieces cut from the rubber imported in the form of "bottles," but his choice of dimensions was necessarily restricted and the pieces obtained in this way were very uneven in thickness. He had previously noted that freshly-cut surfaces tended to unite when pressed together, and he concluded that if he could cut the rubber into a number of small shreds he could form blocks of any suitable size by pressing these shreds together in a mould.

He therefore set about devising some means of shredding the rubber, and eventually constructed a machine consisting of a wooden cylinder studded with teeth revolving in a larger cylinder provided with teeth on the inner surface. When the rubber was introduced between the two toothed surfaces, and the inner cylinder revolved, it was found that instead of the rubber being torn into shreds as was expected, it was converted into a homogeneous plastic mass, heat being generated during the process. Even though the india-rubber were introduced in the form of a number of small scraps, these united to form a single mass.

This was an important development, since by employing this machine, which was first described as a "pickle" and subsequently as a "masticator," he was no longer dependent on the size or shape of the pieces of india-rubber received in this country. By placing the plastic mass produced in this way in a suitable mould and applying pressure, a solid block of any required dimensions could be made. A special machine was subsequently devised by the aid

\* Hancock, p. 14.

† Johnson, E.P. 467, 1853.

of which the block thus formed could be cut into sheets of any desired thickness.

This "cut sheet," as it was and still is called, was adapted to many purposes, surgical appliances, tubing and overshoes being made at an early date.

The beneficial effects of the masticator extended to the preparation of solutions for proofing, Hancock finding that in making a workable solution masticated rubber required only half as much solvent as rubber which had not been so treated.\* (Or, expressed in current scientific phraseology, "the effect of mastication is to reduce the solution viscosity of rubber," a fact which was rediscovered comparatively recently.)

Thus in the years following the application of coal-tar naphtha for preparing solutions and the use of the masticator and cutting machine for making rubber sheet, the development of the industry took place in two main directions: (a) the making of proofed cloth and articles therefrom; (b) the making of articles such as shoes, surgical appliances, etc., from solid sheet rubber.

Although a moderate degree of success was attained in this way, the expansion of the industry was hampered by two pronounced defects from which the manufactured goods suffered. In the first place the surface of the rubber was sticky or "tacky," and, further, the effects of changes in temperature were pronounced, so much so that purchasers of single-texture garments proofed on the inside were warned not to go near a fire, as, on becoming warm, the rubber would adhere to the clothes of the wearer. On the other hand, exposure to cold caused a marked stiffening, and garments in this condition could not be worn with any degree of comfort.

Hancock in England and Charles Goodyear in America devoted their attention to eliminating these undesirable properties. Goodyear in the course of his experiments, which he carried out in the face of considerable financial difficulties, found that treatment with nitric acid produced a change which appeared to be beneficial, but, probably owing to the dangerous character of the operations, this "acid gas process" was not developed to any considerable extent, although a number of promising samples were made in this manner.

Goodyear was chiefly concerned with the removal of the adhesive character of the surface of rubber, and to this end investigated the effect of incorporating various mineral powders, lime and magnesia being tried without success. In 1838 he met Nathaniel Hayward, who had previously employed sulphur for mixing with rubber solutions, and a patent was taken out for the use of a rubber composition containing sulphur as an ingredient.† Articles made with

\* Hancock, p. 11.

† *Gum Elastic*, by Charles Goodyear, New Haven, U.S.A., 1855, Vol. I. p. 112.

such a composition, when exposed to the sun's rays, a process termed solarising, were said to lose their adhesive nature. Later, while heating a composition of rubber and sulphur with which had been mixed some white lead, he was surprised to find that instead of melting, as he had anticipated, the mass became stiffer and bore some resemblance to leather. Goodyear did not patent this invention, but a friend of his who was visiting England gave to Mr. Brockedon, a friend of Hancock's, specimens of rubber prepared by this process without disclosing the manner in which this was carried out. These in 1842 were exhibited to Hancock, who by immersing them in ice found that they did not stiffen as did all other preparations then known. Hancock was satisfied that the object he had in mind could be achieved, but he had no knowledge of how it had been brought about. He resolutely set about the task of discovering the agent responsible for this remarkable change, and prepared numerous compositions of rubber, some of them containing sulphur, all of which he submitted to the action of heat, as he early formed the opinion that heating was a contributory factor in producing the improvement in properties. The test which he applied to the samples after treatment was immersion in ice, and although he tried a considerable number of experiments, he did not meet with any immediate success, as in all cases the low temperature caused stiffening. During the course of his experiments a number of specimens accumulated, and on examining these towards the end of 1843 he noticed that in some cases the appearance suggested that a change had taken place. Although he was at the time unable to say definitely which of the particular ingredients had produced this change, and what degree of temperature was necessary for its occurrence, he shortly afterwards applied for a patent. In the six months' interval between the application and the final enrolment of the specification he vigorously pursued his investigations, in the hope that in the intervening period he would be able to ascertain definitely the conditions necessary for the production of the desired change in the rubber. As he had no means of determining the temperatures to which the various mixtures had been heated, he decided to take as a standard sulphur at its melting point, and consequently immersed strips of cut sheet in a bath of molten sulphur. At first he did not find any alteration in properties other than an apparent absorption of the sulphur by the rubber, but on raising the temperature of the bath somewhat and allowing the strips to remain immersed for a considerable time he found that the change he was hoping for had taken place. Further, he noted that the strips which were left in the sulphur bath for a longer period became dark and horny.

It was clear, then, that sulphur was the agent capable of promoting this

change, and it was equally evident that the action took place only after a long heating at a comparatively high temperature, a circumstance which to some extent explains the failure of many of Hancock's earlier experiments.

Although the first improvement in properties was effected by dipping rubber into molten sulphur, Hancock soon found that equally good results could be obtained by first incorporating the sulphur with the rubber with the aid of his masticator and submitting the compounded material to the influence of heat; this he usually accomplished by suspending the sample inside a high-pressure steam boiler.

In the patent,\* which was duly sealed within the specified time, there is a very comprehensive description of the methods employed for treating "caoutchouc (either alone or in combination with other substances) with sulphur when acted on by heat, and thus changing the character of the caoutchouc."

Hitherto the alteration in properties had been referred to as "the change," and on discussing with his friends the question of adopting some more specific name, Mr. Brockedon suggested the term "Vulcanisation," in reference to the supposed association of the Vulcan of mythology with the employment of sulphur and heat; the process was shortly afterwards described by this name, which is mentioned in patent specifications as early as 1845, and has since been universally adopted.

In works practice, and indeed in technical literature, the term "cure" is frequently employed instead of "vulcanisation." While this has the merit of brevity, it is unfortunately used also to denote the "smoking" of wild or cultivated rubber in the course of its preparation.

In the year following the granting of Hancock's patent, particulars of Good-year's process were made public in this country.† This consisted in employing sulphur in conjunction with white lead, the importance of which lies in the fact that such compositions were capable of undergoing vulcanisation merely by heating in a dry atmosphere at ordinary pressures.

The discovery of vulcanisation removed the chief obstacle to success which had hitherto confronted those who were endeavouring to turn to industrial use the products of the trees in the tropical forests. By its aid the rubber imported in the form of shapeless masses could be converted into a variety of articles which no longer possessed the objectionable sticky surfaces and which did not become stiff when exposed to the influence of cold. Further, the material was changed in a direction that the discoverers had not anticipated, in that the mechanical properties of the rubber were considerably improved.

It is a remarkable fact that the agent which these pioneers discovered is

\* Hancock, E.P. 9952, 1843.

† E.P. 10027 granted to W. E. Newton.

## CHAPTER II

### RUBBER LATEX: ITS COMPOSITION AND PROPERTIES

RUBBER occurs in the vegetable kingdom as a constituent of the latex, a milky fluid, secreted by plants belonging to several botanical orders. The most important rubber-yielding species is *Hevea brasiliensis*, belonging to the natural order *Euphorbiaceæ*, from which at least 98 per cent. of the total production of rubber is obtained. The latex is usually present in a specialised system, of cells or tubes, which extends to all parts of the plant, but those contained in the stem or trunk are the chief source of latex collected for industrial use. The latex cylinders in *Hevea* are situated in the inner portion of the bark next to the cambium, and are arranged in rows the number of which may vary between twenty and forty, decreasing with the height from the ground.\*

### CHEMICAL COMPOSITION

Analyses of latex "obtained from the southern part of Mexico" were made by Faraday,† who ascertained the presence of a hydrocarbon, caoutchouc, together with albuminous matter, wax, a water-soluble substance, and water. Later, the presence of sugar-like substances in latex obtained from various sources was established by Girard,‡ who isolated three distinct substances which he regarded as derived from a sugar, dambose, and to which he gave the names dambonite, bornesite and matezite.

Dambonite, which occurs in Gaboon rubber, melts at 195° C., and is optically inactive. It was investigated by Maquenne,§ by whom it was identified as dimethylinositol,  $C_6H_6(OH)_4(OCH_3)_2$ ; the dambose which was formed on heating with hydrogen iodide was shown to be identical with *i*-inositol.

Bornesite, which was found in Borneo rubber, melts at 199–203° C. and is dextrorotatory,  $[\alpha]_D = 31.16^\circ$ ; it was identified by Flint and Tollens as monomethyl inositol,  $C_6H_6(OH)_5(OCH_3)$ .||

Matezite, found in Madagascar rubber, is an isomeride of bornesite and was

\* Bryce and Campbell, *I. R. J.*, 1917, 53, 721.

† *Quart. Jour. Sci.*, 1826, Vol. 21, No. 41.

‡ *Compt. rend.*, 1868, 67, 820; 1871, 73, 426; 1873, 77, 995.

§ *Ibid.*, 1887, 104, 1853.

|| *Annalen*, 1893, 272, 288.

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shown by Maquenne \* to have the same constitution as  $\beta$ -pinite, which in turn was characterised as monomethyl-*d*-inositol, melting at 186° C. and having  $[\alpha]_D + 65.51^\circ$ .

Later, the presence of monomethyl-*l*-inositol in latex from *Hevea brasiliensis* was ascertained by de Jong,† who established its identity with the compound previously found in quebracho bark and named quebrachitol.‡

Other constituents now recognised to be present besides caoutchouc are proteins, inorganic matter and resin-like substances, generally referred to as the "resins," probably the portion characterised by Faraday as "wax."

Analyses by Beadle and Stevens § of latex from trees of *Hevea brasiliensis*, four years old and ten years old respectively, gave the following figures, calculated as percentages of the original latex :

TABLE I

	Four years old.	Ten years old.
Acetone soluble material (resin) . . . . .	1.22	1.65
Protein . . . . .	1.47	2.03
Ash . . . . .	0.24	0.70
Caoutchouc (by difference) . . . . .	27.07	35.62
Water . . . . .	70.00	60.00

The actual determinations were carried out on the residue obtained after evaporation of the latex ; the acetone-soluble material will in this case probably include inositol derivatives ("sugars"), which are water-soluble, in addition to the resins which are insoluble in water but soluble in acetone.

Subsequent analyses || of the inorganic constituents of three samples gave the following results, calculated as percentages on the original latex :

TABLE II.

	A.	B.	C.
Total Ash . . . . .	0.41%	0.29%	0.24%
Potash ( $K_2O$ ) . . . . .	0.19	0.17	0.14
Magnesia ( $MgO$ ) . . . . .	0.02	0.019	0.008
Lime ( $CaO$ ) . . . . .	0.013	0.014	0.004
Phosphoric Acid ( $P_2O_5$ ) . . . . .	0.13	0.09	0.06
Sulphuric Acid ( $SO_3$ ) . . . . .	0.008	0.009	0.009

\* *Compt. rend.*, 1890, 109, 968.

† *Rec. Trav. Chim.*, 1906, 25, 48.

‡ Tanret, *Compt. rend.*, 1889, 109, 908.

§ *Analyst*, 1911, 36, 6.

|| *Int. Cong. Appl. Chem.*, 1912, 9, 17.

Fresh *Hevea* latex as it exudes from the tree occasionally possesses a faintly alkaline reaction, but according to Beadle and Stevens (*loc. cit.*) this is not invariably the case, as it may be neutral or faintly acid. Acidity quickly develops, however, so that by the time the latex arrives at a locality suitable for testing purposes the reaction is consistently faintly acid. W. Bobilioff, Sr.,\* on examining the latex taken at intervals from a group of fifteen *Hevea* trees ranging from two to twelve years old, did not encounter one instance of alkalinity and obtained a neutral reaction only in a few cases. In general, the reaction was markedly acid, the amount of N. sodium hydroxide solution required to neutralise one litre of latex ranging from 2.5 to 24.8 c.c.

Considerable variations occur in the character and composition of latex obtained from trees of different botanical origin, the chief point of difference being in the relative proportions of caoutchouc and resin present; the rubber obtained from such latices will be associated with the resin originally present, a point to which reference will subsequently be made in considering the various types of raw rubber.

### PHYSICAL PROPERTIES OF LATEX

Latex, especially that from *Hevea brasiliensis*, is usually white in colour and of a consistency approximating to that of cream. Variations in consistency may occur according to the rainfall prevalent in the district in which the tree is growing, and also according to the age of the tree; variations may occur even in trees of the same age situated in a given area.

Latex is a colloidal system in which particles of caoutchouc are dispersed in an aqueous medium. Doubts have been expressed regarding the existence of caoutchouc as such in latex, the contention being that since the suspended particles are liquid they must therefore consist of some simpler hydrocarbon which is polymerised to caoutchouc during coagulation.† On somewhat similar grounds there is a divergence of opinion concerning the designation of latex as an emulsion or as a suspension,‡ according to whether the caoutchouc, even if present as such in the latex, is to be considered as a liquid or a solid. On examination under the microscope the suspended particles in fresh latex appear as spherical or pear-shaped globules exhibiting Brownian movement. The size of the globules varies in *Hevea* latex from 0.5–2.0 $\mu$  in diameter, although

\* *Archief*, 1919, 3, 408.

† Weber, *Gummi Zeit.*, 1903, 17, 296; for the contrary view see Hinrichsen and Kindscher, *Ber.*, 1909, 42, 4329.

‡ Cf. Twiss, *J. Soc. Chem. Ind.*, 1919, 47 T.

sometimes smaller or larger ones are observed;\* the particles in the latex of *Funtumia elastica* are smaller, the average diameter being  $0.5\mu$ .

The specific gravity of *Hevea* latex is on an average 0.99, but is dependent upon the rubber content and also upon the nature and proportion of the dissolved substances present in the serum. While the rubber content of latex varies considerably, the specific gravity of the serum is as a rule fairly constant.†

Proposals have frequently been made for arriving at the rubber content of latex from a determination of the specific gravity. Vernet,‡ for example, drew up a series of tables correlating the rubber content of latex with the specific gravity. Eaton has devised a "latexometer," a form of hydrometer, and worked out a scale indicating the corresponding rubber content. The specific gravity of latex will be dependent on the relative proportions of rubber having a specific gravity of 0.913 and serum having a specific gravity between 1.0226 and 1.0170.§ Although it had been previously suggested that the relationship between specific gravity and rubber content was not a linear one, de Vries concluded that this was true only in the case of latex which had been diluted, and that with undiluted latex the specific gravity varied directly as the rubber content. Even when employed for standardising latex which has been diluted, in accordance with plantation practice, it is possible that useful comparative results may be obtained, as Stevens || quotes a case in which the "Metrolac" hydrometer (introduced by the Rubber Growers' Association) had been used for a year and a difference of only 1 per cent. noted between the rubber content as given by the instrument and the actual output of rubber.

### Coagulation.

The process by which rubber is generally obtained from latex is that of coagulation, which takes place as a result of the fusion of the globules of rubber present in the latex to form larger masses. The clot formed in this manner is usually referred to as the "coagulum," the aqueous portion being designated the "serum." Beadle and Stevens,¶ in a study of *Hevea* latex, recognised three types of aggregation, viz. creaming, flocculation, and coagulation proper. Creaming is due to the formation of aggregates of a comparatively small number of globules; the cream after separation may be dispersed by shaking and the original latex is apparently reconstituted. Microscopic examination shows this is not the case, however, as the individual particles are seen to have collected in groups, and Brownian movement no longer persists. In curdling or floccula-

\* Bobilioff, *Archief*, 1919, 3, 374.

† *Le Caout. et la G. P.*, 1910, 4558.

|| *Bull. R. G. A.*, 1919, 1, 44.

† de Vries, *ibid.*, 1919, 3, 183.

§ de Vries, *loc. cit.*

¶ *Int. Cong. Appl. Chem.*, 1912, 9, 35.



tion the aggregates are much larger and may be seen to resemble flocks or curds. Normal coagulation, such as is effected by treatment on the plantations, is characterised by the formation of a compact clot. According to Schidrowitz \* the globular form persists in the rubber after coagulation, an observation which might argue in favour of the rubber being present in the latex as a solid. This view receives further support from the observation of Beadle and Stevens (*loc. cit.*), that the aggregates present irregular appearances in the case of *Hevea* latex. On the other hand, in the fusion of the globules of *Ficus* and *Castilloa* latices smooth aggregates are formed as from the union of liquid or semi-plastic particles.

Coagulation may occur as a result of heating, formation of a cream by gravitation, addition of suitable reagents, or as a consequence of the occurrence of natural changes. Each of these methods is applied to the preparation of one or other of the different kinds of wild rubber, and will be considered in detail when dealing with the particular variety to which the process may be applicable.

Most latices will coagulate on heating, especially if allowed to stand for some time after issuing from the tree. The gravitational method, on the other hand, is applicable only to certain kinds of latex; the process may be likened to the separation of cream from milk, and the phenomenon is, in fact, usually referred to as "creaming." The latex from *Castilloa elastica* and from *Ficus elastica* is specially susceptible to creaming, and the process may be hastened by dilution with water or by centrifugalising; the "cream" may be removed as a pasty mass which dries to a transparent sheet of rubber.

Coagulation by addition of reagents is the method most usually adopted in the case of plantation rubber, and is also the basis of many native methods for obtaining wild rubbers.

It is an interesting fact that the same reagent is not effective for all latices. For example, latex from *Hevea brasiliensis* is readily coagulated by addition of acid, even small proportions of acetic acid (3 c.c. per litre of latex) sufficing for complete coagulation. On the other hand, *Funtumia elastica*, *Ficus elastica* and *Castilloa elastica* are not coagulated by acid, but this may be effected by agents which will not coagulate *Hevea*; thus the addition of formaldehyde to *Funtumia* latex causes coagulation,† whereas this is effectually prevented when the same reagent is added to *Hevea* latex.

The majority of latices will coagulate gradually if allowed to stand, and, in the absence of special precautions, the process is accompanied by putrefactive changes.

\* *J. Soc. Chem. Ind.*, 1909, 28, 6.

† Schidrowitz and Kaye, *ibid.*, 1907, 26, 1264.

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Various theories have been propounded regarding the underlying causes of coagulation. The neutralisation of the electrical charge on the suspended particles has been suggested as a possible explanation. Spence has shown,\* however, that in the case of *Funtumia* and *Hevea* latices the electrical charge is the same, since on passing a current the globules migrate towards the positive pole; nevertheless these behave differently in presence of acid which causes coagulation of *Hevea* but not of *Funtumia*.

In the opinion of Fickendey † latices are emulsions rendered stable by the presence of protective colloids which may be either proteins or peptones. Dilution of the latex will result in lowering the concentration of the protective colloid and rendering the emulsion unstable, hence "creaming" will take place. Alternatively, addition of a suitable precipitant for the particular colloid present will similarly cause coagulation to take place. In support of this theory Fickendey points to the presence of peptones in *Funtumia* latex, which is coagulated by means of peptone precipitants such as formalin, but is not affected by acids. On the other hand, *Hevea* latex, which contains protein, is coagulated on addition of a protein precipitant but not by formalin.

It may be noted that the results refer to coagulation as normally practised, that is to say, using small proportions of the coagulating agent. As Whitby has shown ‡ in the case of *Hevea* latex, the addition of hydrochloric acid, for example, in small proportion produces coagulation, but on increasing the proportion of acid a point is reached when coagulation ceases; further addition produces no effect until at a certain concentration coagulation again takes place. It is quite conceivable that at these higher acid concentrations the forces in operation differ from those at the lower concentrations, and indeed in this case the effect may be similar to that produced by the addition of acid to a negatively charged colloidal suspension. The existence of protein or allied substances in latex has long been known, and in the early part of last century Lüdersdorff referred to the particles in latex as being enclosed in an albuminous envelope.§ A similar view was later adopted by Weber,|| who regarded coagulation as being due to the protein being rendered insoluble in the course of which the rubber globules were enclosed within the precipitated protein meshwork. Although not accepting the view regarding the existence of a protein envelope, Vernet,¶ after reviewing all existing theories of coagulation, concludes by attributing it to precipitation of protein.

A hypothesis which has lately received much support is that which attributes

\* *I. R. J.*, 1908, **36**, 233.

† *Ibid.*, 1913, **12**, 147.

|| *Ber.*, 1903, **36**, 3108.

† *Koll. Zeit.*, 1910, **8**, 43.

§ Cf. *I. R. W.*, 1922, **67**, 137.

¶ *Le Cabut. et la G. P.*, 1919, **16**, 9835.

coagulation to the action of an enzyme present in the latex, the effect being similar to that produced by the addition of rennin to cows' milk.

This view is the outcome of a study of the natural or spontaneous coagulation of latex, which Spence \* originally thought was due to the influence of acids formed from the carbohydrate constituent of latex by an oxidase.

A somewhat similar conclusion was arrived at by Eaton and Grantham,† who attributed the coagulation to lactic acid produced from the carbohydrates not by an enzyme but by bacterial action.

Whitby,‡ however, had shown that coagulation took place equally well in absence of air, and concluded that there was present in the latex in addition to oxidase a specific coagulating enzyme.

Evidence in support of the enzyme theory was afforded by some experiments of Campbell,§ who found that addition of small proportions of calcium salts accelerated coagulation; the significance of this observation lies in the fact that the presence of calcium salts is known to favour the activity of clotting enzymes. Further, coagulation was retarded by the addition of small proportions of calcium precipitants, such as neutral potassium oxalate, to fresh latex, which contains calcium salts.

Barrowcliff || again showed that *Hevea* latex (sterilised by running slowly into boiling water) did not coagulate on addition of acetic acid, but if a few drops of fresh latex were first added, coagulation proceeded normally. Similarly, sterilised latex allowed to stand in an open vessel did not coagulate even after some days, although it was in a room opening on to a plantation and presumably liable to bacterial infection; addition of fresh latex, however, caused coagulation to take place within twenty-four hours. Further, the addition of toluene, a known bactericide, did not inhibit coagulation, whereas hydrocyanic acid, which is generally fatal to enzymes, prevented coagulation. These experiments, together with later ones of Whitby,¶ argue in favour of an enzyme

rather than a bacterium being the prime cause of coagulation; at the same time it may be noted that bacteria are present in *Hevea* latex, Vernet and \*\* having characterised no fewer than twenty-seven different types of organisms, only one of which is anaërobic.

Those who adopt the view that a specific coagulating agent is present in latex, thus accounting for the coagulation taking place spontaneously, regard the coagulation by addition of acid as being due to the same enzyme, the activity

\* *on India-Rubber*, 1908, p. 198.

*Bull. F. M. S.*, 1915, 4, 26; see also Eaton, *ibid.*, 1917, 6, 156.

., 1913, 45, 941.

1918, 37, 48 T.

*out. et la G. P.*, 1920, 17, 10491.

§ *J. Soc. Chem. Ind.*, 1917, 36, 274.

¶ *Agric. Bull. F. M. S.*, 1918, 6, 374.

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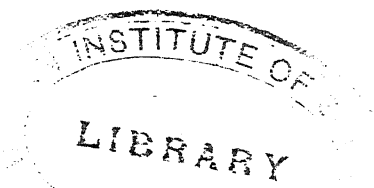
of which is stimulated by the acid. Conversely the addition of alkalis would be expected to inhibit the action of the enzyme, and this is in accord with known facts, since alkalis generally are employed as "anti-coagulants," that is to say, agents which are added to latex in order to prevent spontaneous coagulation. It may be pointed out that latex which is exported is usually treated previously with an anti-coagulant such as ammonia, the addition of which permits of its transportation over long distances without coagulation taking place. Consequently in investigations carried out in Europe or any locality outside the rubber-growing area, such "preserved" latex must necessarily be employed. It has been pointed out by several workers that results obtained in this manner are apt to be misleading, as the characteristics of the subsequent coagulation are not entirely comparable with those of fresh latex.\*

\* Beadle and Stevens, *Int. Cong. Appl. Chem.*, 1919, 9, 17; De Vries, *Archief*, 1923, 7, 198.

1496

6782

1122



## CHAPTER III

### SOURCES OF RUBBER : WILD RUBBER

#### *South America. Para Grades*

ALTHOUGH at the present time the greater proportion of the world's supply of rubber comes from the plantations of the Far East, appreciable quantities are still obtained from uncultivated trees indigenous to certain tropical countries.

The most important source of such wild rubber is the country around the mouth and the valley of the river Amazon in South America. The producing trees belong to the genus *Hevea*, and the species yielding the best quality of rubber is *Hevea brasiliensis*, from which is obtained the well-known Para rubber, so called because of the fact that the chief port of shipment is Para (Belem), situated at the mouth of the Amazon. This part of the river is studded with islands, and the rubber collected in the surrounding country is known as "Islands" or "soft cure" Para, a name referring to the appearance of the rubber after coagulation by smoking or "curing." \* Rubber coming from the country surrounding the upper reaches of the Amazon is called "Up-river" or "hard cure" Para, designations which may be further qualified according to the country of origin by prefixes such as Peruvian, Bolivian, Acre, etc.

Although the producing trees are wild forest growths the collection of the rubber is carried out on a carefully elaborated system by individuals or corporate bodies, who, after selecting a suitable site, must first get it surveyed by a State official.

When a concession is obtained the lessees erect huts for the workers, and through the forest paths are cut, each of which, starting and finishing at one of the huts, embraces an area known as an estrada, containing perhaps fifty trees.

The general method of obtaining the latex from the tree is by tapping, which is usually performed by the labourer making a number of incisions

\* The term "curing" is also used to denote the change known as vulcanisation (see p. 19), but is not used in this sense in the present instance.

in the bark with the aid of an instrument resembling a small hatchet, a tin cup being fixed to the tree immediately below the cut, in order to collect the latex which gradually exudes. The tapper proceeds from tree to tree, tapping each in succession, until he arrives back at the starting-point; he then goes the round once more and transfers the latex which has collected in the cups to a suitable receptacle, finally arriving back at the hut. The latex which has been obtained during the day is ready for coagulation, and this is accomplished by exposing thin layers to the smoke made by a fire, which is fed with palm nuts in districts where these are plentiful, or with wood. Over the fire is placed a cone-shaped pipe of earthenware or sheet-iron which serves to localise the smoke, and then into the latex is dipped a long pole or paddle around the end of which has been wound a piece of rubber which has already coagulated. The latex adheres and forms a film, which is held in the smoke until most of the moisture has dried out, the operation being then repeated again and again, the bulk of rubber gradually increasing in size with each dipping. When the amount of rubber coagulated renders the dipping operation difficult the pole is supported by means of a rope slung from the roof of the hut, and the latex is carefully poured on to the mass, the process being continued as before until a ball of rubber, somewhat elongated, is obtained which may be 24 inches in length, 18 inches in diameter and 100-120 lbs. in weight; in some cases the biscuits are much larger and may weigh as much as 5 cwt. This ball or biscuit is removed from the wooden core, and in this form comes on the market, constituting the well-known grade "Fine Hard Para," which for many years was the standard to which all other grades of rubber were referred. It will be seen that the process is in effect one of evaporation,\* and the rubber will contain most of the constituents of the original latex and will still retain a proportion of moisture constituting from 16-18 per cent. of the total weight.

Sometimes latex drops from the paddle during the process of building up the biscuit and a certain proportion coagulates on the sides of the vessels employed. These scraps may be introduced into the ball, and on account of their thickness do not dry out as completely as the rest, consequently remaining as wet patches in the finished biscuit; if the latex has dropped on to the ground, the coagulated mass will also be contaminated with earth, wood chips, etc. Such rubber is regarded as an inferior grade and is usually known as "Entrefine" or "Medium Fine" Para. These contaminations

\* From the comparatively low proportion of ash obtained on incineration and of water-soluble material present in unwashed Para rubber, it is not unlikely that a part of the serum is lost by exudation during the building up of the biscuit, so that the process is not entirely an evaporative one.

are not apparent on examining the outside of a complete biscuit, but if this is cut into two pieces longitudinally the section at once shows the presence or otherwise of wet patches or of foreign matter. At the big rubber centres in the Amazon country it is customary to cut up in this manner and assign to the particular grade all the biscuits before they are exported, and thus the rubber manufacturer receives these Para grades in the form of half-biscuits, with a depression along the cut surface showing where the pole or paddle on which the rubber is coagulated has been withdrawn. In the case of "Hard Fine" Para the biscuit will be seen to be built up of regularly disposed concentric layers of rubber of one inch or so in thickness, each of which represents one day's collection and smoking. These thick layers are in turn made up of innumerable thin layers formed from each successive coating of latex; these thinner layers are not easily detachable, but the thicker layers can generally be separated comparatively readily. The rubber usually appears opalescent owing to the presence of a small proportion of moisture which has not been evaporated. The "Hard Entrefine" will contain white opaque, spongy masses, perhaps possessing an unpleasant odour, and contaminated in some cases with particles of foreign matter. Scraps of self-coagulated rubber from latex cups, pails, etc., which are not put into the biscuits, are air-dried, then collected together and made up into irregular balls, in which form they are known as "Sernamby," "Coarse Para," or "Negroheads," and of course do not possess the characteristic odour which is conferred on the other grades by the process of smoking.

The bulk of the rubber prepared in the district round the mouth of the Amazon is not dried to the same extent during the smoking process as is the up-river grade, and the finished biscuits consequently contain a larger proportion of moisture; the biscuits are therefore of a somewhat spongy character and are marketed as "Soft Cure" Para.

"Weak Fine" Para is the name given to the somewhat inferior rubber obtained from species of *Hevea* other than *Hevea brasiliensis*.

#### *Other South American Grades*

Other rubber-yielding trees indigenous to South America are those belonging to the genus *Castilloa*, and the rubber known as "Centrals" is obtained from the species *Castilloa elastica*, which flourishes in the country north of the Amazon, and also in some parts of Mexico in Central America. The methods of collecting the latex and obtaining the rubber therefrom differ from those practised in the case of *Hevea* trees. In the first place the latex, instead of being collected in cups, is allowed to flow from the incision made

in the bark, down the tree trunk and then into a cavity in the ground which may be lined with a palm leaf. Coagulation of the latex is then induced by adding a decoction of the stems of the amola vine or other astringent plant, and sometimes by means of soap solution. The rubber settles out in the form of a slab, and after drying is marketed in this condition. That portion of the rubber which coagulates and dries in the incisions and on the trunk of the tree is collected and sold as "strip."

*Castilloa Ulei*, which grows in Bolivia, Peru, and most of the rubber-producing areas in Brazil, furnishes the grade known as "Caoucho," which may be in the form of slab, strip or ball.\* The collection of the rubber involves the destruction of the tree. A broad V-shaped cut is made near the base of the tree, and when the latex, which is collected in a suitable vessel, has ceased to flow, the tree is cut down and incisions passing right round the trunk are then made at intervals of about two feet. The further quantities of latex which gradually exude are collected and coagulated in a manner similar to that described in the case of *Castilloa elastica*. The portion which coagulates in the incisions round the trunk is allowed to dry in the air and is then stripped off and made up into balls constituting the Caucho Ball of commerce.

Another South American tree worthy of mention is *Manihot Glaziovii*, which grows in the State of Ceara, Brazil, and which yields the Ceara or Maniçoba rubber. The tree flourishes in districts where the rainfall is low, and as a consequence the flow of latex on tapping is very scanty. Owing to the low proportion of water present coagulation takes place rapidly, and in fact usually occurs as the latex flows from the incision, so that the rubber collects on the bark in the form of large drops of a characteristic amber colour. The coagulated rubber is stripped from the tree and with the adherent bark comes into the market as Ceara Scraps. In districts where rainfall is higher the latex may be fluid enough to reach the ground before coagulating, in which case it is collected in a hole made for the purpose, coagulation taking place on standing.

#### *African Rubbers*

At the present time comparatively little wild rubber is collected outside South America; indeed the total output from such sources does not constitute as much as 1 per cent. of the world's production (see Table IV, p. 40).

Most of the wild African rubber is obtained from plants belonging to the natural order *Apocynaceæ*, of which the genera *Funtumia*, *Landolphia* and *Clitandra* are the most important. Of the genus *Funtumia*, the chief rubber-yielding species is *Funtumia elastica*, a forest tree which sometimes reaches

\* H. C. Pearson, *I. R. W.*, 1910, 43, 7.



a height of 100 feet and which is found in Sierra Leone, Togoland, Nigeria, the Cameroons, French and Belgian Congo, Uganda, and the East Africa Protectorate. Other species of *Funtumia* yield latices which, however, contain little or no rubber.

The general method of obtaining the latex consists in tapping the tree by making incisions with a gouge-like instrument, the incisions usually extending a considerable distance up the trunk, so that it is necessary for the collectors to employ slings or stagings for climbing to the required height. The latex is coagulated either by allowing to stand, when clotting gradually occurs, or the latex may be heated, when coagulation takes place rapidly. A third method is to add infusions prepared by boiling the leaves or twigs of certain plants which probably owe their activity to the presence of tannic acid.\* The rubber obtained from *Funtumia elastica* comes into the market generally in the form of slabs, lumps, balls, etc., and is named according to the country of origin, *e. g.*, Cameroon Ball (which may also be from *Landolphia* species), Benin lump, or Lagos "silk rubber," so called on account of the peculiar sheen which it exhibits when cut with a knife.

The greater proportion of African rubber, however, is obtained from the *Landolphas*, which are large vines or creepers indigenous to a wide area of tropical Africa, notably to French Guinea, Angola, French Senegal, the Cameroons, and the French and Belgian Congo. The most important species is *Landolphia owariensis*, from which is prepared the bulk of the Congo rubber; this is characterised by possessing a somewhat reddish colour.

*Landolphia Heudelotti*, from which Gambia, Konakry and Soudan rubbers are obtained, is also widely distributed, and of the less abundant species *Landolphia Kirkii* and *Landolphia Klanei* may be mentioned. The methods employed for obtaining rubber from the vines resemble those previously described, the latex being allowed to coagulate spontaneously in the incisions made in the stems, or the latex is collected and coagulated either by boiling or by adding plant juices. Methods involving the destruction of the plant are also practised, the stems being cut into suitable lengths, and the latex which exudes collected and coagulated; in the case of smaller growths, the whole plant may be dug up and allowed to dry, the rubber which coagulates *in situ* being subsequently separated from the bark by a process of maceration.

#### *Eastern Rubbers*

The only rubber-producing species which is at all frequently met with in Asia is the *Ficus elastica*, belonging to the natural order *Urticaceæ*. It is

\* Christy, *I. R. J.*, 1909, 37, 400.

found growing wild in Assam, Rangoon, Burma, Java, Straits Settlements, and the Federated Malay States, the rubber obtained from the latter districts being known as Rambong. In some cases the latex coagulates almost immediately after issuing from the cuts made by the tapper, and the rubber is then stripped from the tree stem and comes on the market with adherent bark. Where the latex flows freely enough to be collected it does not coagulate at all readily and it is necessary to stir it vigorously with a paddle. Coagulation may, however, be hastened by adding latex which has already been thickened in this manner and which is known as "bibit." \*

An inferior rubber which in the days of high rubber prices became of importance industrially is that known variously as Jelutong, Gutta Jelutong, Pontianac, Bresk, or Dead Borneo, which is obtained from the *Dyera costulata*, a large tree growing in Borneo, Sumatra and Malaya. The native method of coagulating the latex is by the addition of kerosene together with gypsum, and the material thus obtained is a white mass which after drying contains a large proportion, sometimes as much as 75 per cent., of resinous matter, the remainder consisting of rubber. The crude material is usually marketed without previous purification, but some years ago a large plant was erected in Sarawak, Borneo, for the purpose of "deresinising," or extracting the resinous matter from the crude product, and putting on the market the comparatively pure rubber thus obtained.† This deresinised jelutong was actually sold in the open market and realised prices very little below those ruling at the time for Para rubber, but with the decline in rubber prices generally the manufacture became unprofitable, and operations were suspended in 1913. The crude resin-containing material, however, is still produced in small quantities.

#### *Mexican Rubbers. Guayule*

The rubber known as Guayule is obtained from the *Parthenium argentatum*, a shrub belonging to the natural order *Compositæ*, and is found in Mexico and Texas. Its mode of occurrence in the plant differs essentially from that which obtains in the types of rubber hitherto described. In these instances the rubber is obtained from the milky juice or latex which flows from the tree on making incisions in the bark. In the Guayule plant, however, the latex is present in separate cells in the stems from which there is no exudation on cutting.‡ The plant must therefore either be dug up or cut off near the roots in order to secure the rubber. There are two processes available for the separation of the rubber from the woody fibre, and of these the mechanical

\* A. Van Gelder, *Tropenpflanzer*, 1911, 15, 651. † Schidrowitz, *I. R. W.*, 1911, 43, 130.

‡ Lloyd, *ibid.*, 1910, 41, 115; 1913, 48, 563.

process is probably the most important. This consists in macerating the shrub with water in a crusher and passing the pulp into a type of ball mill, when agglomeration of the rubber takes place and the fibre is then washed away. The rubber may be submitted to a further process of purification by boiling with caustic soda, which removes a proportion of the resinous matter with which it is associated. The alternative method consists in extracting the shrub with suitable solvents and subsequently precipitating with alcohol or evaporating to obtain the rubber. The proportion of rubber calculated on the dried plant is 10 to 15 per cent. Although Guayule was known to exist in Central America in the middle of last century, it was not until 1902 that attempts were made to utilise the rubber on a large scale. In that year a factory was erected at Jimulco for dealing with the shrub, and by 1905 rubber obtained from this source was placed on the market. Other factories were erected, and the industry developed extremely rapidly until 1910, when production began to decline.

TABLE III  
IMPORTS OF GUAYULE RUBBER INTO NEW YORK

Year.	Tons.
1907	2992
1908	3850
1909	8674
1910	10,656
1911	8091
1912	6105
1913	2756
1914	850
1915	2217
1916	1133
1917	140
1918	1329
1919	1501
1920	1037
1921	58
1922	281

The diminished output is to a large extent traceable to the practice of cutting down the shrub, as a result of which the available supplies have been very materially reduced, although attempts have been made to cultivate the plant in certain districts.\*

Guayule rubber is of a blackish-green colour and possesses a pronounced

\* Lloyd, *loc. cit.*

aromatic odour due to the resinous matter with which it is associated; the "deresinised" material, however, is almost odourless.

*Other Sources of Rubber*

Apart from the above-mentioned varieties of rubber, all of which have been, and indeed still are to a greater or less extent, utilised industrially, there are known a number of plants containing rubber which has hitherto not been extracted on a commercial scale. Among these may be mentioned *Chrysothamus nauseosus*, or "rabbit brush," which grows in western parts of North America, and in which the rubber, designated "Chrysil," is contained in separate cells as in the case of Guayule, the proportion found varying from 2 to 3 per cent. calculated on the dry shrub.\* This and other similar plants have been investigated very thoroughly at the instance of the United States Government in order to ascertain whether it is possible to create a reserve of rubber in the event of overseas supplies being cut off.

\* Hall and Goodspeed, *I. R. W.*, 1920, 61, 203.

## CHAPTER IV

### SOURCES OF RUBBER: PLANTATION RUBBER

ALTHOUGH there are enormous reserves of rubber trees in South America alone, their inaccessibility renders the gathering of the produce a costly undertaking. In addition, parts of the country are very sparsely populated; in the Brazilian State of Matto Grosso, for example, with an area of over a million square miles, the number of inhabitants does not exceed 150,000,\* and conditions are not such as to attract labour from outside.

It is true that attempts have been made from time to time on a small scale to plant *Hevea* trees in the more accessible regions of the Amazon country, and in 1883 a private estate at Santarem was planted with a few thousand trees which were tapped with satisfactory results ten years later.†

The possibility of cultivating rubber in selected areas was one that attracted attention some considerable time ago. Hancock himself, writing in 1855,‡ refers to the fact that he had already "called attention to the possibility of cultivating the best kinds of caoutchouc-bearing plants in the East and West Indies." "From the best information I have been able to obtain there is every probability of success, and, as this substance is now become an article of large and increasing consumption, plantations of these trees may, in a few years, produce a beneficial return."

About the year 1870 the proposal to cultivate rubber was seriously considered by the India Office, acting on the advice of Sir Joseph Hooker, Director of Kew Gardens, and instructions were given to obtain seeds and plants for this purpose. *Hevea brasiliensis* was decided upon as the most suitable species for cultivation, and from a small consignment of seeds secured by Mr. James Collins in 1873 a dozen plants were raised at Kew, but these did not reach Calcutta alive. Subsequently, an open commission was given to Mr. (afterwards Sir) Henry Wickham, a planter at Santarem, who collected together 70,000 seeds and was fortunate enough to secure a steamer without cargo which he loaded with his seeds. Under the guise of "rare botanical specimens" these were successfully got past the authorities at Para, and arrived in Liverpool

\* I. R. W., 1910, 43, 5.

† *Ibid.*, 1910, 43, 46.

‡ Hancock, p. 34.



PLATE 2.—PARA RUBBER TREES ONE YEAR OLD.

## SOURCES OF RUBBER: PLANTATION RUBBER 39

in June 1876 in good condition. From this consignment 2800 plants were raised at Kew, about 2000 of which were sent to the Botanic Gardens at Paradeniya, Ceylon. A proportion of these were subsequently sent to Perak, in Malaya, and seven were planted at Kuala Kangsar, a further lot of twenty-two being sent to Singapore. In both cases the plants flourished and seeds were produced as early as 1881; these were planted in various districts, and it soon became evident that the climate of Malaya was eminently suited to the growth of the *Hevea* tree. In spite of the good results which these early experiments promised, the idea of cultivating rubber on a large scale did not at first appeal to planters, so that by 1902 there were only 4500 acres in Ceylon and 16,000 acres in Malaya under rubber. Small lots of rubber were, however, forwarded to the London market from time to time and were able to command prices very little below those ruling at the time for Fine Hard Para.

In the meantime planting had been commenced on a small scale in the Netherlands Indies, and has since developed considerably both in Java and Sumatra; the cultivation of rubber has also been introduced in Southern India, Burma, British Guiana, Belgian Congo, Nigeria, the Cameroons and in other areas to which it is indigenous, but the industry has not developed to such an extent as in the other countries mentioned.

The best results have been obtained in most cases with *Hevea brasiliensis*, even in districts where the indigenous plants belong to other botanical orders; certain species such as *Funtumia elastica* and *Castilloa elastica* have, however, been planted with success in Africa and Mexico respectively.

The rapid expansion of the rubber-planting industry and the relative production of plantation and wild rubbers will be evident from the table on p. 40.\*

Every effort has been put forth both by the various Governments concerned and by the planting companies themselves in order to assist in the establishment of the industry, and in the production of a grade of rubber which will give satisfaction to the manufacturers of rubber goods. In Ceylon and in the Federated Malay States the Government have scientific staffs whose advice is at the disposal of planters, and the Rubber Growers' Association, a body comprising a large proportion of the British planting companies, maintains an organisation of its own, besides having a consulting chemist in this country. The Dutch planters have provided similar facilities for the plantations in the Dutch East Indies, and maintain a research station at Buitenzorg, in Java, from which is issued a journal embodying the experimental results obtained. As a consequence there has grown up an extensive literature relating to the cultivation and preparation

\* *The Rubber Position*, Rickinson, London.

TABLE IV

	Total Acres Planted.	Rubber Produced (Tons).			Total.
		Wild.			
		Plantation.	Brazil.	All Others.	
1905 . . .	116,500	145	35,000	27,000	62,145
1906 . . .	294,200	510	36,000	29,700	66,210
1907 . . .	506,550	1,000	38,000	30,000	69,000
1908 . . .	687,350	1,800	39,000	24,600	65,400
1909 . . .	861,150	3,600	42,000	24,000	69,600
1910 . . .	1,122,550	8,200	40,800	21,500	70,500
1911 . . .	1,505,350	14,419	37,730	23,000	75,149
1912 . . .	1,817,350	28,518	42,410	28,000	98,928
1913 . . .	2,021,750	47,618	39,370	21,452	108,440
1914 . . .	2,181,050	71,380	37,000	12,000	120,380
1915 . . .	2,293,750	107,867	37,220	13,615	158,702
1916 . . .	2,458,950	152,650	36,500	12,448	201,598
1917 . . .	2,611,350	213,070	39,370	13,258	265,698
1918 . . .	2,759,950	255,950	30,700	9,929	296,579
1919 . . .	2,910,750	285,225	34,285	7,350	326,860
1920 . . .	3,020,750	304,816	30,790	8,125	343,731
1921 . . .	3,069,750	271,233	19,837	2,890	293,960
1922 . . .	—	355,340	21,755	3,205	380,280

of rubber, and there are a number of books available dealing in considerable detail with this branch of the rubber industry.

A short outline of plantation procedure may here be given, and brief reference made to some of the more important factors which exert an influence on the yield and character of the rubber produced.

When the site for the plantation has been selected and cleared of all growth, seedlings about six months old—in certain cases the seeds themselves—are planted at suitable intervals, usually in regular formation so that the trees will be from twenty to thirty feet apart, and arranged in rows which may be spaced at similar distances. Originally the planting was much closer, the trees in each row being about ten feet apart, the same distance separating the rows, giving a total of over 400 trees per acre as compared with 110–130 per acre usually adopted at the present time.





PLATE 3.—TAPPING RUBBER—SINGLE CUT.

## TAPPING

The trees will be ready for tapping to commence at four to six years of age, by which time the height may be about 30 feet and the girth 18 to 24 inches at 3 feet from the base. The tapping is usually accomplished by carefully excising a thin strip of the bark with the aid of a special knife, the cut travelling obliquely round a quarter of the circumference of the trunk. The latex, which gradually exudes, flows along the surface of the cut and is conducted into a porcelain or glass cup by means of a metal spout fixed to the tree (see Plate 3). The strip of bark removed at each tapping is approximately 0.04 inch wide, and the same operation is repeated daily, in some cases on alternate days, the next strip being removed immediately below the other, so that after twenty-five tappings approximately 1 inch of the bark measured vertically will have been removed. After tapping has been in progress for a certain period, say one year, another quarter circumference of the trunk, usually the opposite, not the adjacent, quarter, is operated upon, and in this way the tapping of the original portion of the trunk is commenced again after a three years' rest. Instead of one-quarter, one-half or one-third of the circumference may be selected for tapping. While this system is the one most favoured at present, other systems are still in vogue to a greater or less extent. Of these the basal V is the one which is most frequently used. In this case two oblique cuts are made in the shape of the letter V near to the base of the tree, and the latex is collected in the usual way (see Plate 4).

Other systems which are now practically obsolete are the herring-bone, in which a number of oblique cuts are made at intervals in the form of V's connected by a central channel (see Plate 5), and the half herring-bone in which only one-half of the V is cut (see Plate 6).

The latex, which comes from the cuts in the form of a creamy liquid, continues to flow for perhaps one to two hours, the amount collected varying considerably even in trees in the same locality. Not only may the yield of latex vary, but the rubber content of latex from a number of trees may differ widely, as has been shown by Whitby,\* who found that in a population of 245 seven-year-old trees in the Malay States, the latex contained from 23 grm. to 55 grm. of rubber per 100 c.c., the average being 36.58 grm. In a population of 1011 trees in the same area the yield of rubber per tree varied from 1 to 43 grm. per day, with an average of 7.12 grm. Similar results have been obtained in Java by de Vries.† In the case of a particular tree eleven years old, which was regarded as a good yielder, the amount of rubber latex collected

\* *I. R. J.*, 1919, 58, 895.

† *Comm. Cent. Rubber-station, Buitenzorg*, 1922, No. 29.

per day varied from 46 to 206 c.c. over a period of one year; the rubber content of the latter ranged from 33.7 to 44.7 per cent., and the yield of rubber per day from 20.6 to 74.9 grm.

Factors such as the age of the tree and the number of trees per acre also influence the yield and rubber content of the latex.

### COAGULATION

The latex which collects in the cups is emptied into pails, the last traces being washed out with water and the somewhat diluted latex afterwards transferred to large wheeled tanks and conveyed to the central station, where it is to be coagulated (see Plate 7). In order to prevent premature coagulation of the latex, it is customary to add to the contents of the pails certain reagents known as "anti-coagulants," those most commonly in use being sodium sulphite, formaldehyde, ammonia, and sodium carbonate. The latex, which, in the course of the above operations, has been diluted so that its rubber content is approximately 20 per cent., is first strained to remove gross impurities and is then transferred to large bulking tanks, a procedure which ensures that the output of the estate shall be uniform in colour and in other respects (see Plate 8). After diluting to a standard rubber content the latex is run into smaller tanks, where coagulation is effected by adding acetic acid in the proportion of 0.3 part per 100 parts latex.

Other coagulating agents have been employed or suggested, as, for example, formic acid, fermented coconut juice ("toddy"), hydrofluoric acid (known as Purub), sulphuric acid ("Coagulatex") and alum, which at one time was much used on native holdings in Malaya, but is now prohibited by law. Passing carbon dioxide into latex was at one time said to bring about coagulation,\* but it was subsequently shown that this was actually caused by the fine spray of hydrochloric acid from the apparatus in which the gas was generated. It has also been proposed to effect coagulation by passing an electric current through the latex,† Henri having shown‡ that the rubber particles are negatively charged and will therefore collect round the anode.

In the absence of any special precautions fresh latex will coagulate spontaneously (see p. 28), and if air is excluded the coagulation will be unaccompanied by putrefactive changes: a method of effecting such anaërobic coagulation on a commercial scale, known as the M.C.T. process,§ has been

\* W. Pahl, E.P. 26173, 1910.

† T. Cockerill, E.P. 5854, 1910; 21441, 1908; P. S. Clignett, *Le Caout. et la G. P.*, 1915, 8721.

‡ V. Henri, *Compt. rend.*, 1907, **144**, 431.

§ Introduced by Maude, Crosse, and Thomas, E.P. 104323, 1916; for a description see M. Barrowcliff, *J. S. C. I.*, 1918, **37**, 95 T.

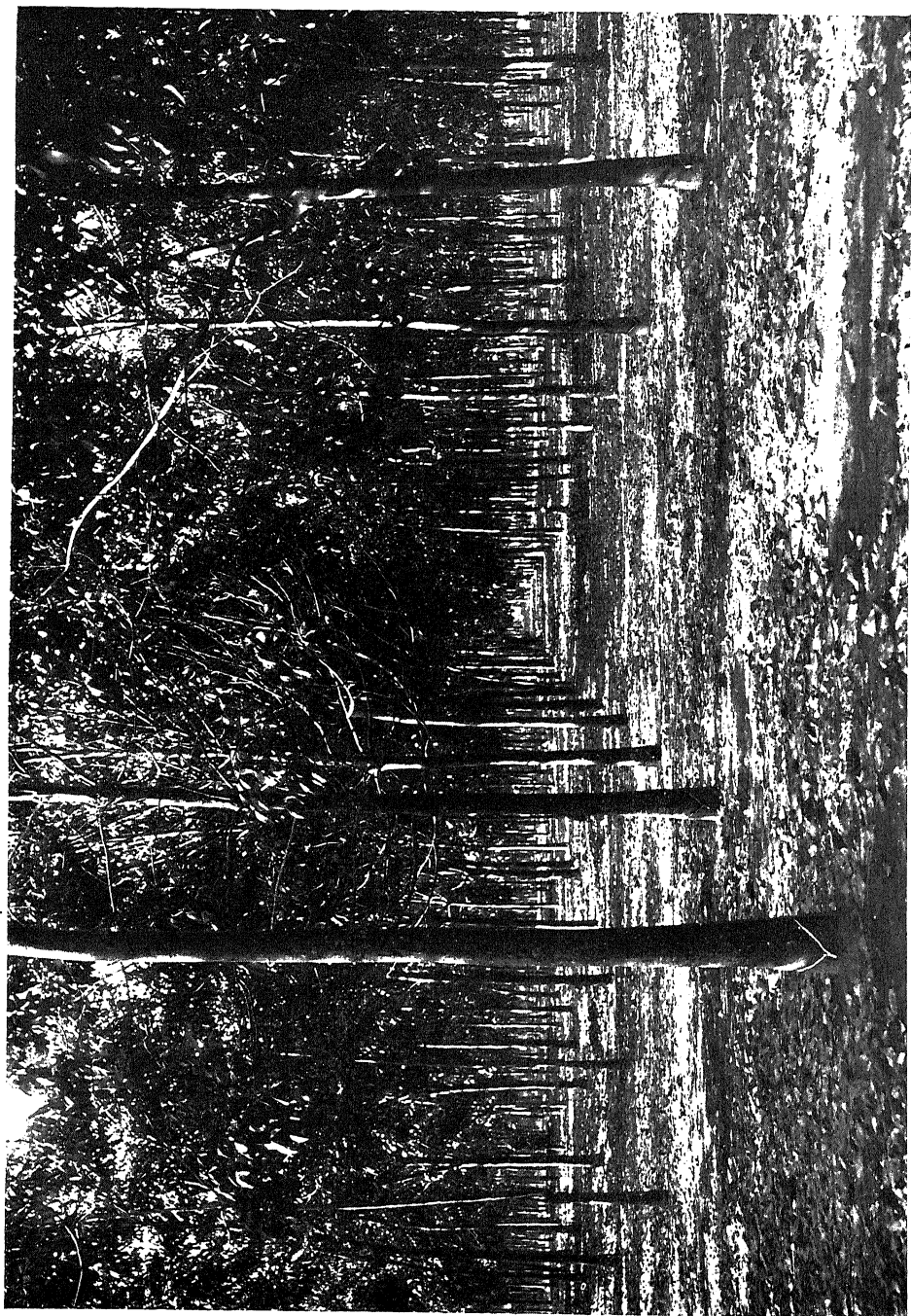


PLATE 4.—GENERAL VIEW OF A RUBBER ESTATE. BASAL V-TAPPING.

## SOURCES OF RUBBER: PLANTATION RUBBER 43

devised. The coagulation may be hastened by the addition of soluble calcium salts or sugar.\*

Another method, which is chiefly of theoretical interest, consists in exposing latex in a refrigerator and allowing it to remain in a frozen condition for some hours, when, on thawing, it will be found to have coagulated.

Centrifugal separation may be resorted to in the case of certain latices,† notably those from various *Castilloa* species, but is not suitable for general use with *Hevea* latex.

The Ilcken-Down process,‡ in which coagulation is induced by the addition of a mixture of alcohol and petrol or coal-tar naphtha, has been claimed to give higher yields of rubber, but although the method has been submitted to critical examination, no evidence in support of this statement has been adduced.§

In all the above methods the rubber is separated from the latex by means of a process of coagulation, the "serum" or liquor remaining after removal of the rubber retaining certain organic and inorganic constituents originally present in the latex. In the case of Para rubber, however, the method of separation is partly one of evaporation, although this is doubtless accompanied in some measure by coagulation which may result in loss of serum by exudation.||

The extent to which this may occur is not certain, but it may be taken that rubber so prepared in the Amazon country contains, if not all, at any rate an appreciable proportion of the original constituents of the latex. The undoubtedly high quality of the Para rubber has frequently been attributed to the mode of preparation, and numerous processes have been patented for the treatment of latex on the plantations, in which the principles involved in this method have been embodied.¶

In most cases the latex is delivered on to a revolving drum or travelling belt and the thin film exposed to the action of a heated and smoke-laden atmosphere, thus affording a close approximation to the conditions under which the Para rubber is prepared. It has been shown, however, that in reality the method of coagulation by acetic acid yields as good a rubber as that prepared from the same latex by the Brazilian method.\*\*

\* B. J. Eaton, *Bull. F. M. S.*, No. 27, p. 276.

† *I. R. J.*, 1910, 39, 652.

‡ E.P. 8487, 1915.

§ Eaton, *Bull. F. M. S.*, No. 27, p. 272; de Vries, *Comm. Central Rubber-station, Buitenzorg*, 1921, No. 21.

|| Cf. footnote, p. 31; also de Vries, *Estate Rubber*, 1920, p. 415.

¶ Wickham, E.P. 7371, 1907; 2627, 1914; Freudweiler, E.P. 19784, 1911; Derry, E.P. 6858, 1911; ten Houte de Lange, E.P. 24342, 1913.

\*\* G. S. Whitby, *J. S. C. I.*, 1916, 35, 493.

A process of partial evaporation under reduced pressure followed by exposure to acetic acid vapours or smoke has also been suggested.\*

None of the processes enumerated, however, has proved successful on a commercial scale, either on account of the cost or because of the failure to yield a product superior to that which may be obtained by coagulation with acetic acid. Nevertheless, much interest has been aroused recently by the Hopkinson process, which has much in common with these, consisting as it does in projecting latex in the form of a fine spray into a chamber through which a current of heated air or inert gases is passed.† The finely divided latex loses its moisture rapidly and the rubber left after evaporation falls to the bottom of the chamber in the form of particles resembling snow, containing all the original constituents of the latex; the rubber prepared in this way is referred to as L.S., *i. e.* latex-sprayed, rubber.

It is too early yet to foresee whether the process will ultimately find application on a large scale, but it is probable that the value of such a method of treatment will lie not so much in the superiority of the rubber produced as in the saving of power effected by curtailing the milling period incidental to the manufacturing operations (see p. 200), since the compounding ingredients may be added previous to the latex being evaporated.

While the various other methods of preparing rubber from latex are not without interest, it is probable that at least 90 per cent. of the rubber produced on the plantations at the present day is obtained by coagulating with acetic acid.

The addition of acetic acid causes the gradual formation of a clot which falls to the bottom of the tank as a thick spongy slab which contains a considerable proportion of water, and on this account is opaque and almost white in colour.

This "coagulum" is then subjected to treatment, the nature of which depends on the form in which the rubber is to be put on the market.

#### GRADES OF PLANTATION RUBBER

Rubber prepared from latex which has been collected, strained, and coagulated under supervision is referred to as "First Latex" rubber, to distinguish it from grades made up of scrap or of rubber formed as a result of accidental coagulation either in the collecting cups or other vessels employed on the estates. First latex is usually marketed either in the form of "smoked sheet" or "pale crêpe," which are the highest grades of plantation rubber and are most in demand.

In the earlier days of the plantation industry the bulk of the rubber was

\* N. W. Barritt, E.P. 3632, 1914.    † Hopkinson, E.P. 157978; *I. R. J.*, 1923, 65, 89.





PLATE 5(A).—TAPPING—HERRING-BONE  
SYSTEM.



PLATE 5(B).—TAPPING—HALF HERRING-  
BONE SYSTEM.

prepared in the form of "biscuits," circular slabs obtained by coagulating in shallow pans; this grade has now almost entirely disappeared.

*Slab Rubber.*—If the coagulum is deprived of excess of serum by passing between rollers without appreciably reducing the thickness and then allowed to dry spontaneously, there is formed what is known as slab. This type of rubber has been made chiefly in connection with experimental work (see p. 139), and until recently has not been prepared on an extensive scale for ordinary industrial purposes. It is now coming into favour, especially with American manufacturers, and particularly with those who possess their own estates and who can thus prepare their rubber in the way they desire. Slab rubber is usually characterised by possessing an unpleasant odour due to the occurrence of putrefactive changes, and by retaining in the interior a considerable proportion of serum, the exterior surfaces only being relatively dry and transparent.

*Smoked Sheet.*—The sheet rubber made on estates owned by the larger companies is almost invariably prepared by a process of smoking. In making sheet rubber coagulation is carried out in partitioned tanks (see Plate 9), the coagulum being obtained in the form of slabs of a definite size and thickness. These are passed between rollers revolving at even speeds, so that the bulk of the adherent serum is removed, the thickness of the slab being reduced in the process. In this way sheets are formed approximately 24 in.  $\times$  15 in. and about  $\frac{1}{8}$  in. thick. In some cases the sheets are allowed to remain smooth, but frequently they are finally passed between rollers engraved in a suitable manner, a diamond or ribbed pattern being much favoured. These patterns thus provide projections, so that when the sheets are packed for transport there is not the same tendency to adhere to form a compact mass as is the case with smooth sheets. After rolling, the wet coagulum is hung in a special smoke-house in which is burning a fire made with wood, coconut husks, or other available fuel. The rubber is thus dried in a smoke-laden atmosphere at a temperature of approximately 110° F. At this comparatively high temperature drying takes place more rapidly than in the case of the unsmoked sheet and may be completed in ten days.

During the smoking process the rubber acquires a colour varying from amber to a rich reddish-brown, and the finished sheet possesses a characteristic odour resembling that of Brazilian Para rubber. The brown colour is said to be due to compounds formed by oxidation of the phenolic constituents of the smoke accelerated by the oxidase present in the rubber. The most important effect of smoking is to render the rubber more resistant to the development of mould growths on the surface than in the case of unsmoked sheet, and instances of mould formation on smoked sheet are comparatively rare.



In the normal smoking operation the drying and smoking take place simultaneously; a modification, known as the Byrne process, has been patented in which the wet coagulum is exposed to smoke for some hours and subsequently dried in air at ordinary temperatures. In some cases the "Byrne-cured" rubber is marketed in the form of slab containing a considerable proportion of moisture in the interior. The smoke is produced by dropping a mixture of specially supplied liquids, apparently crude acetic acid and wood tar, on to a hot plate. Such "Byrne-cured" rubber has been prepared by certain estates, but its adoption has not been at all general, as the rubber obtained in this way does not possess any marked advantages over normal smoked sheet.\*

*Unsmoked Sheet.*—The production of unsmoked sheet is almost entirely confined to small holdings owned by natives, and in such cases the machinery available is of a primitive character. Consequently, the sheet is almost invariably in the smooth condition when marketed, as distinct from the smoked sheet which is usually passed between engraved rollers to give it a raised pattern.

Drying is usually carried out in the open air, or less frequently in well-ventilated sheds at ordinary tropical temperature. Under these conditions drying proceeds comparatively slowly and may require three or four weeks for completion.

An objection to the production of unsmoked sheet is that in the course of preparation the rubber is not submitted to a washing process, and consequently will contain a proportion of the serum constituents; the presence of these on the surface is favourable to the development of mould growths, thus detracting from the value of the rubber in the open market.

*Pale Crêpe.*—The term crêpe is applied to the type of rubber produced by passing the wet coagulum between rollers revolving at uneven speeds, during which operation a stream of water is made to impinge on the rubber; the material is thus made into a continuous sheet with a broken surface and bears some resemblance to ordinary crêpe fabric (see Plate 10). The effect is usually produced by passing successively through a series of "mills," as they are termed, which are adjusted so that the distance between the rollers decreases from the first to the last. The surfaces of the rollers are usually scored or engraved, markedly so in the first and to a lesser degree in the succeeding mills; in this way the coagulum is readily broken down from a lump until it is finally obtained in the form of crêpe of any desired thickness. For ordinary purposes the thickness is usually less than  $\frac{1}{16}$  in., when it is called "thin crêpe," but sometimes a thicker material is required, in which case it is termed "blanket crêpe"; latterly there has been a demand for an even thicker material, especially

\* *Bull. Imp. Inst.*, 1916, 14, 539; *Eaton, Bull. F. M. S.* No. 27, p. 267.

## SOURCES OF RUBBER: PLANTATION RUBBER 47

for making soles for footwear, and this "sole crêpe" may be  $\frac{1}{2}$  in. or more in thickness. Crêpe, especially the thinner varieties, is usually dried at ordinary temperatures, and the operation is complete in a much shorter time than is the case with sheet, owing to the greater surface exposed by a given weight. Crêpe made from first latex is usually prepared in the form of what is known as pale crêpe, an almost white opalescent material obtained by treatment of the latex with sodium bisulphite before coagulation. Under ordinary circumstances the coagulum which at first forms is practically colourless, but on drying darkens considerably, owing to oxidation of non-caoutchouc constituents accelerated by the presence of an oxidising enzyme.\* It has been found that, by adding sodium bisulphite to the latex, before coagulation, in the proportion of 1 part per 400 or less, sufficient of the reagent is retained by the coagulum to inhibit the action of the oxidase during the drying of the crêpe; under these conditions darkening does not take place.† Such pale crêpe contains sodium sulphite when it comes on the market, and objections have been raised that the properties of the rubber are adversely affected by its presence; this view is, however, no longer held, as it has been shown by various workers that the rubber is not in any way deteriorated by the traces of sulphite retained. The reason for preparing rubber in this way may not appear at all obvious, as the original colour is not of great importance. Since, however, rubber is generally bought from the estates by brokers who judge the material by outward appearance only, the growers have sought to make their produce as attractive as possible. The attitude of the brokers is not wholly unreasonable, since, in the case of this pale crêpe, any carelessness in preparation or presence of dirt or other foreign matter would be evident.

It has been shown that in the preparation of crêpe the coagulum is subjected to the action of a stream of water during its passage through the mills; as a result, practically the whole of the serum is washed out, and in this respect crêpe differs from sheet, which retains a proportion of the serum. Crêpe, therefore, is not so liable to be attacked by mould as is unsmoked sheet, and on this account the smoking of crêpe is rarely resorted to. Moreover, the effect of smoking would be to darken the crêpe, and in this state it would be indistinguishable from the lower grades which are described below.

*Brown Crêpe.*—During the operations of collecting latex, transferring it to transport cans and handling generally, a certain proportion undergoes coagulation, and in this way scraps accumulate which dry spontaneously and darken. These scraps may be made into crêpe, which will be inferior to pale crêpe only in respect to colour.

\* Spence, *I. R. J.*, 1911, **41**, 93.

† Beadle, Stevens, and Morgan, *ibid.*, 1913, **46**, 222.

*Lower Grades of Crêpe.*—In addition to the scraps just referred to, which contain very little in the way of gross impurities, there will also be found on the tapping cuts, on the bark of the tree, and even on the ground, scraps of rubber to which earth and other foreign matter may adhere. In addition, through exposure to the sun some pieces may have developed tackiness. This scrap is collected and submitted to a process of washing at the crêping mills, and in this way a considerable proportion of the impurities will be removed. The crêpe made up in this way will still contain particles of earth, wood, etc., and consequently commands a somewhat lower price than the better grades.

Although the production of these lower grades cannot be avoided, at least 80 to 85 per cent. of the total output of a well-managed estate \* should consist of "First latex" rubber, the remainder comprising lump rubber, which is made into brown crêpe (2 to 4 per cent.), scrap and bark rubber (9 per cent.), and earth scrap (1 per cent.).

\* Eaton, *I. R. J.*, 1921, 61, 286.



PLATE 7(A).—BULKING LATEX.

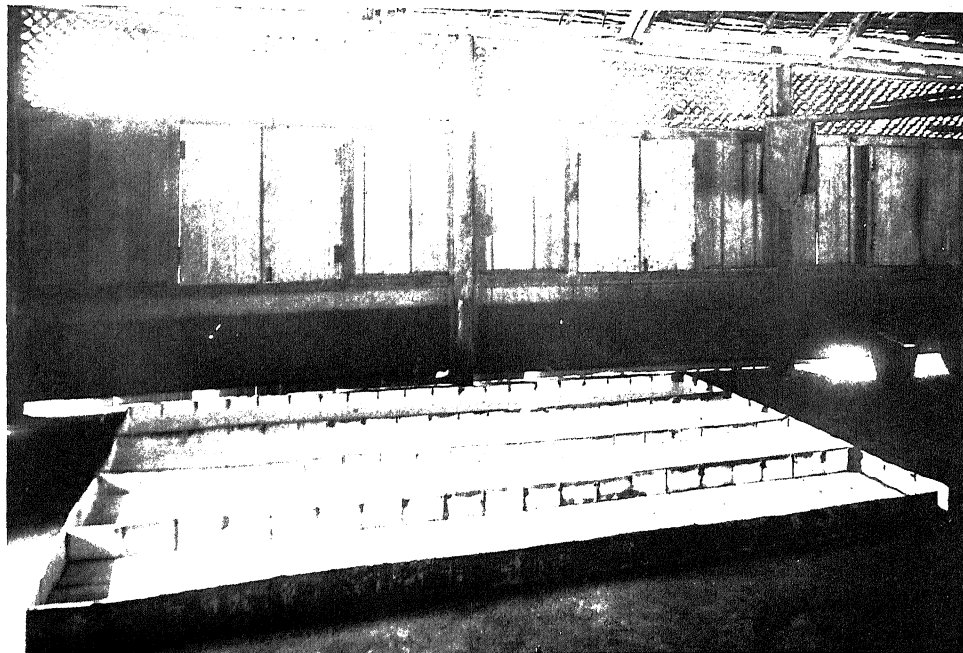


PLATE 7(B).—SHEET COAGULATING TANKS.

## CHAPTER V

### COMPOSITION OF CRUDE RUBBER

THE raw rubber of commerce owes its characteristic properties to the presence of the hydrocarbon caoutchouc, which, however, is invariably associated with greater or less proportions of other substances originally present in the latex. These consist of (a) resin-like substances; (b) nitrogenous substances; (c) inorganic matter; (d) carbohydrates. These constituents, if present in normal amounts, are not to be regarded as undesirable impurities, but, as will be shown later, their presence contributes materially to satisfactory working of the rubber during manufacturing operations.

#### *Resins*

If finely comminuted rubber is extracted with certain liquids in which the caoutchouc portion is insoluble, acetone being the one which is most commonly employed, there is obtained on evaporation an amorphous residue which is generally termed the "resin." This varies in consistency from a soft mass in the case of plantation or Para rubber to a hard, brittle solid in the case of jelutong. The percentage content of resin varies according to the botanical origin of the rubber, but is remarkably constant for each particular species. The following table gives typical analyses of rubbers, many of which, however, are not used industrially at the present time.

TABLE V

Type of Rubber.	Resins per cent.
Plantation Sheet Smoked . . . . .	2.5- 3.5
" " Unsmoked . . . . .	2.5- 3.0
Plantation Pale Crêpe . . . . .	1.8- 3.0
Hard Fine Para . . . . .	3.0- 3.5
Evaporated Latex . . . . .	5.0- 6.0
Ceara Scrap . . . . .	3.0- 5.0
Cameroon Ball . . . . .	7.0-10.0
Guayule (untreated) . . . . .	13.0-18.0
Jelutong (Pontianak) . . . . .	70-80
Lagos Lump . . . . .	10

Very little is known regarding the chemical composition of the resins present in the better grades, such as Para or plantation rubber, but Cohen \* succeeded in isolating from an African rubber of high resin content a white powder which on crystallising from acetone yielded prismatic needles melting at 235° C., having  $[\alpha]_D - 83.7^\circ$  in chloroform solution; this was subsequently identified as  $\beta$ -amyrin acetate. From the same resin there was obtained a body closely resembling the isocholesterol obtained by Schultze from wool fat, and the complete identity of these two substances was subsequently established.†

In an investigation on jelutong resin Cohen ‡ showed that the substance previously isolated and described as alstol by Sack and Tollens § was in reality a mixture of  $\alpha$ - and  $\beta$ -amyrin acetates. Lupeol was also isolated and its benzoate (m. p. 273° C.), acetate (m. p. 218° C.) and cinnamate (m. p. 249° C.) prepared and characterised; the presence of lupeol and of amyrin acetate in jelutong was subsequently confirmed by Hillen.||

A systematic study of the resins from various rubbers made by Hinrichsen and Marcusson ¶ revealed the interesting fact that of the samples examined only those from *Hevea* rubbers were optically inactive, the remainder being dextro-rotatory, guayule resin having  $[\alpha]_D + 12.5^\circ$  and jelutong  $[\alpha]_D + 50.1^\circ$ . The behaviour towards  $\frac{N}{2}$  alcoholic potassium hydroxide was also investigated, and it was found that the resins possessing high optical activity contained high proportions of unsaponifiable matter, Para resin containing 15 per cent., guayule 78.2 per cent. and jelutong 100 per cent.

The iodine values of the resins were also determined and found to be for Para 118, guayule 94.1 and jelutong 30.6.

The behaviour of certain resins on saponification has also been investigated by Terry,\*\* Schidrowitz and Kaye,†† and Ellis and Wells,‡‡ who state that 95 per cent. of jelutong resin is unsaponifiable, and by Dekker,§§ who found in the resins from hard fine Para 25.4 per cent., plantation sheet 48.3 per cent., plantation crêpe 22.0 per cent. and jelutong 83.2 per cent. unsaponifiable matter.

Resins have frequently been referred to as products of oxidation of caoutchouc, but the constancy of the proportion of resin present in a particular variety of rubber does not lend support to this theory. Apart

\* *Arch. Pharm.*, 1908, **246**, 515.

† *Rec. Trav. Chim. Pays. Bas.*, 1909, **28**, 368.

‡ *Arch. Pharm.*, 1913, **251**, 94.

\*\* *J. S. C. I.*, 1889, **8**, 173.

†† *J. Ind. Eng. Chem.*, 1915, **7**, 747.

† *Ibid.*, 1908, **246**, 592.

§ *Ber.*, 1904, **37**, 4110.

¶ *Z. angew. Chem.*, 1910, **23**, 49.

‡‡ *Ibid.*, 1907, **26**, 129.

§§ *Delft Comm.*, p. 249.

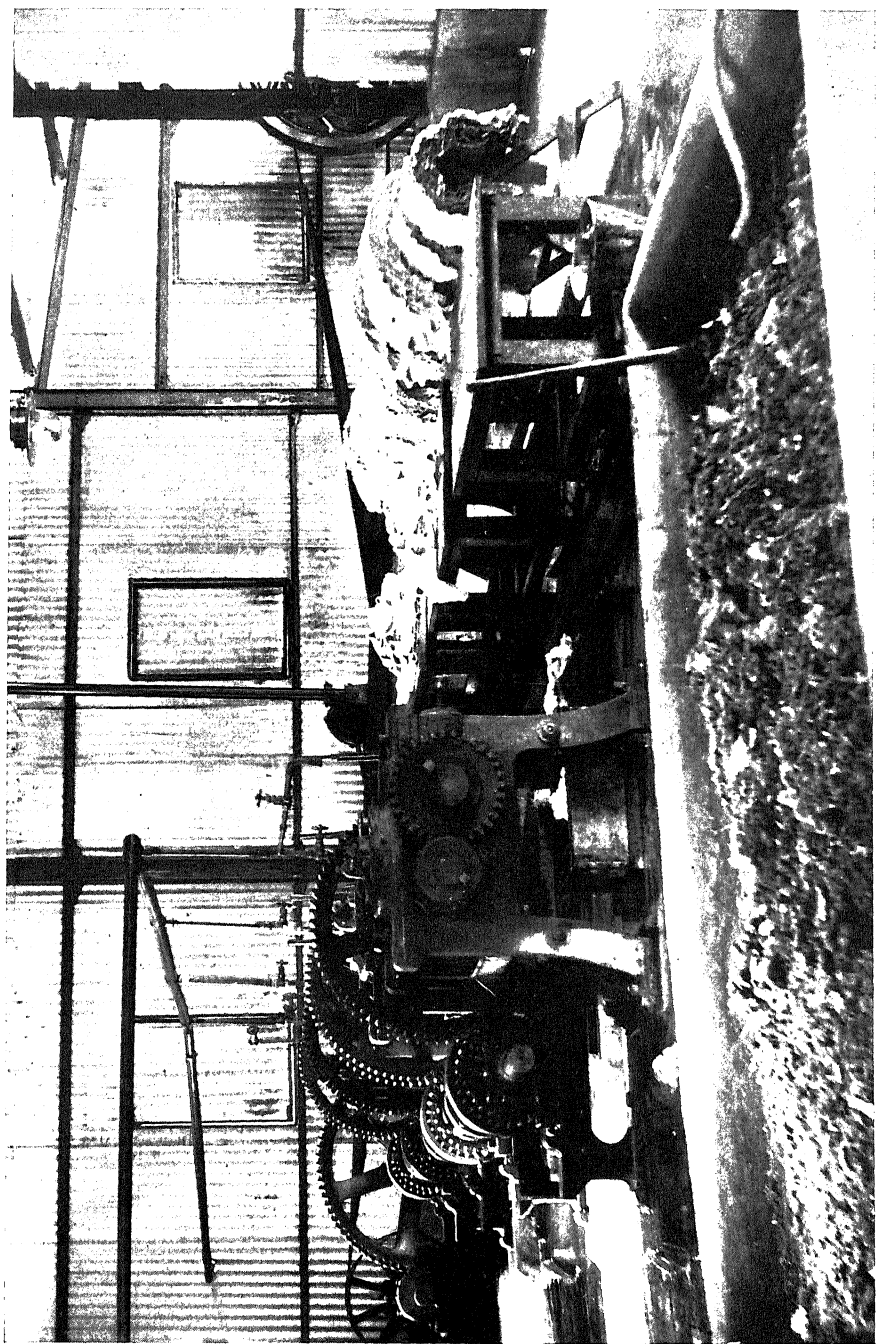


PLATE 8.—CRÉPING MACHINES.

from this, caoutchouc does not exhibit a tendency to oxidise at all readily under normal conditions, and even when oxidation is induced there is little similarity between the products of oxidation and the naturally occurring resins. Terry (*loc. cit.*) found the bromine absorption value for oxidised caoutchouc to be 129, a figure considerably higher than that for resins of Para or African rubbers, which gave values of 46 and 80 respectively. Hinrichsen, Marcusson and Quensell \* showed that the product obtained by the oxidation of caoutchouc previously freed from resin was optically inactive, whereas the resin originally present was dextro-rotatory, so that in the case of rubbers other than *Hevea* at least a portion of the resin, the optically active constituent, is not an oxidation product.

These observations do not entirely preclude the possibility of the optically inactive resins in *Hevea brasiliensis* rubber resulting from a process of oxidation, but the experiments of Dekker (*loc. cit.*) show that whereas oxidised rubber is almost entirely saponifiable, the resins from plantation sheet contain 48.3 per cent. and plantation crêpe 22 per cent. of unsaponifiable matter; further, the writer's experience is that whereas oxidised caoutchouc is invariably hard and brittle, the resin from *Hevea* rubbers is usually quite soft.

### NITROGENOUS MATTER

The occurrence of a nitrogen-containing substance in rubber latex was noted by Faraday,† and later its presence in Para rubber was demonstrated by Gladstone and Hibbert,‡ who found that on treating with chloroform the rubber slowly dissolved, leaving a sort of network of a nitrogenous body which in one experiment constituted 4 per cent. of the whole weight. Spence § subsequently found that this insoluble material consisted mainly of protein and contained up to 5.4 per cent. of nitrogen; its mode of distribution through the rubber in the form of fibre-like threads was demonstrated by photomicrographs of sections stained with silver nitrate solution. Owing to the viscous nature of the rubber solutions considerable difficulty may be experienced in separating the nitrogenous material from the caoutchouc portion, and in order to facilitate its isolation and estimation various methods have been proposed for bringing about a reduction in the viscosity of the rubber solutions. Beadle and Stevens || suggested heating the rubber in phenetole or nitrobenzene and pouring the solution into a large volume of benzene and allowing to settle, while Frank's method ¶ consisted in boiling in cymene,

\* *Z. angew. Chem.*, 1911, **24**, 725.

† *Quart. Jour. Science*, 1826, **21**, 19.

‡ *Trans. Chem. Soc.*, 1888, **53**, 679.

§ *Inst. Comm. Res. in Tropics*, Liverpool Univ., Reprint No. 13, 1907.

|| *Analyst*, 1912, **37**, 13.

¶ *Rubber Industry*, London, 1914, 144.



centrifuging, reboiling and washing successively with benzene and ether. Spence and Kratz \* found that the addition of 0.5 per cent. of trichloroacetic acid to a rubber solution caused a very marked reduction in viscosity and that on warming the process was accelerated. Later, Bernstein † succeeded in producing a similar effect by exposure to ultra-violet light in a sealed tube from which air was excluded. From these mobile solutions the nitrogenous matter may be readily separated and washed by decantation and in this way freed from adherent rubber. The insoluble constituent isolated from different samples of plantation rubber by Spence and Kratz contained nitrogen in proportions varying from 9.83 to 12.08 per cent., and exhibited the characteristic behaviour of a glucoprotein, giving reactions for both proteins and carbohydrates. On this account it was held that the method previously proposed for determining nitrogenous material in rubber, namely, the estimation of the percentage of nitrogen and multiplying by 6.25, the usual factor for proteins, ‡ led to incorrect results, and it was suggested that a factor of 10 should be adopted.

The nitrogenous constituent from different samples of Fine Hard Para contained from 7.75 to 10.3 per cent. nitrogen, and was of a very stable character, as it gave reactions for proteins only after hydrolysis, in this respect differing from that obtained from plantation rubber. Nevertheless Spence and Kratz regarded the two substances as being similar in character, and concluded that neither was a simple protein.

The proteid character of the nitrogenous constituent was further emphasised by Frank (*loc. cit.*), who showed that the material responded to the biuret, xanthoproteic, lead sulphide and Millon's reactions, and that on hydrolysis there were formed monoaminocarboxylic acids, aromatic amino acids, tryptophane and cystin.

### INOSITOL DERIVATIVES

While the latex of *Hevea brasiliensis* and other rubbers contains carbohydrates, the proportion of these present in the rubber will depend on the method of preparation. In the case of rubber prepared by the Brazilian method or by other processes involving complete or partial evaporation of the latex, the whole or a considerable proportion of the original constituents may be retained by the rubber; but where ordinary coagulation processes have been employed the bulk of the water-soluble constituents will remain in the serum and only a small proportion pass into the coagulum. Pickles

\* *Koll. Zeit.*, 1914, 14, 262.

† *Ibid.*, 1914, 15, 49.

‡ Cf. Schmitz, *Gummi Zeit.*, 1913, 27, 1085, 1131.

and Whitfeild,\* however, have isolated from both Brazilian and plantation *Hevea* rubber a crystalline sugar-like substance melting at 191–192° C. and having  $[\alpha]_D - 80^\circ$ . This was found to have the formula  $C_6H_{11}O_5OCH_3$  and was identified as *l*-methyl inositol (quebrachitol), the presence of which in the aqueous portion of *Hevea* latex had already been noted by de Jong (*loc. cit.*).

### MINERAL CONSTITUENTS

As a general rule plantation rubber retains only a comparatively small proportion of the mineral constituents present in the latex, but the amount may vary according to the method of preparation. Thus samples prepared by special processes involving evaporation of the latex will contain the whole of the original inorganic constituents, and there may also be present salts, as, for example, sodium sulphite, which have been used as anticoagulants on the estate. Such samples may contain from 1.2 to 1.8 per cent. of mineral matter as determined by the ash left on ignition.† Plantation sheet or crêpe usually leaves from 0.2 to 0.4 per cent. ash, and the writer has not met with higher percentages than these even in samples of slab rubber which is not washed after coagulation. Brazilian Para rubber contains somewhat higher proportions, the average being in the neighbourhood of 0.5 per cent.

In exceptional cases the rubber may be contaminated with sand, earth, etc., but the presence of such gross impurities may be readily detected on examining the ash microscopically.

The composition of the inorganic portion of rubber latex has already been referred to (Table II, p. 23).

\* *Chem. Soc. Proc.*, 1911, 27, 54.

† *Delft Comm.*, 2, 52.

## CHAPTER VI

### PHYSICAL PROPERTIES OF RAW RUBBER

EXCEPTING in certain special instances, rubber finds industrial application only after its properties have been modified by the process of vulcanisation. The behaviour of vulcanised rubber is therefore of greater moment than that exhibited by the raw material, and will be discussed in detail in a subsequent chapter. The physical properties of unvulcanised rubber, therefore, have not been investigated so thoroughly as have those of the vulcanised material, except in cases where it is possible to correlate these properties with those exhibited after vulcanisation.

In general, unless otherwise stated, the facts here presented relate to rubber containing the accessory substances usually present, and not to specially purified samples. As a rule, however, the varieties which in the natural state are the purer chemically, as, for example, Para or plantation rubber, are chosen by experimenters, and in these cases the behaviour will be very similar to that of the principal constituent.

Rubber is a transparent, distensible substance which may be obtained almost colourless and odourless. The density varies slightly according to the origin of the sample, the value for smoked plantation sheet being between 0.915 and 0.930.

#### ACTION OF SOLVENTS

The caoutchouc portion of rubber is not dissolved by alcohol or acetone, but in certain other liquids, such as carbon disulphide, carbon tetrachloride, chloroform, or benzene, the rubber gradually swells and is finally dispersed, forming a viscous colloidal "solution." Some types of rubber, notably Para rubber, do not dissolve completely, but there remains a portion which gradually settles out as a flocculent mass consisting chiefly of the nitrogenous or "insoluble" constituent previously referred to. It has frequently been stated that this behaviour is characteristic of rubber, no matter what the origin or method of preparation, but there are certain types of plantation rubber which invariably dissolve in benzene to give clear bright solutions \* in which insoluble

\* Cf. Schidrowitz and Goldsborough, *J. S. C. I.*, 1909, 28, 3.

matter is not discernible. In the writer's experience rubber obtained by the spontaneous evaporation of preserved latex, rubber coagulated by the anaërobic method, and slab rubber usually give such clear solutions in benzene, although when petroleum ether is employed a part remains insoluble. Caspari \* has examined the behaviour of rubber in different solvents, and states that an apparently clear solution such as is obtained with benzene in reality contains undissolved matter which is not visible on account of its transparency in this particular solvent. When petroleum ether is employed, however, the insoluble matter is clearly seen and can be collected. This insoluble portion Caspari regards as consisting wholly or in part of a caoutchouc-like body, and not entirely of protein, from which he concludes that rubber is really of a composite character and that there are present two hydrocarbons of the same empirical formula. Of these one is soluble in most rubber solvents, whereas the other, which he terms the "pectous" form, does not dissolve, but swells to a marked extent in carbon tetrachloride, chloroform and carbon disulphide, to a lesser degree in benzene, and least of all on immersion in paraffin hydrocarbons. This pectous form was isolated from different kinds of rubber and was found present to the extent of 88.1 per cent. in a sample of Acre Para rubber, 40.5 per cent. in Ceylon biscuit, and 11.2 per cent. in a sample of Malayan crêpe. These results have, however, been criticised by Stevens,† who has carried out a series of experiments, from the results of which he concludes that the action of petroleum ether differs only in degree from that of other solvents, and that on continued treatment the pectous portion dissolves almost entirely, leaving only a small residue which consists of nitrogenous matter.

Even though it is not possible by means of solvents to effect a separation of caoutchouc into two hydrocarbons of the same empirical formula, this does not necessarily preclude the possibility of the existence of two such phases. Indeed, rubber probably consists of an emulsoid system in which both the disperse and continuous phases are modifications of the same hydrocarbon in different states of molecular complexity.‡ The fact that rubber which is transparent at ordinary temperatures becomes stiff and opaque at low temperatures is regarded by Twiss as confirmatory evidence of the existence of two phases.§

The rate of solution of raw and purified rubber in various solvents has been studied by Ditmar,|| whose experiments showed that carbon disulphide was the most effective for bringing rubber into solution, other liquids being

\* *J. S. C. I.*, 1913, 32, 1041.

† *Ibid.*, 1919, 38, 192 T.

‡ Cf. Ostwald, *Koll. Zeit.*, 1910-6, 136; Potts, *The Chemistry of the Rubber Industry*, London, Constable, 1915, p. 39.

§ *Ibid.*, 1919, 38, 48 T.

|| *Gummi Zeit.*, 1905, 19, 578, 608.

in the following order: chloroform, ether, toluene, carbon tetrachloride, benzene and petroleum ether. These results were arrived at by shaking a known weight of the rubber in a definite volume of the solvent, withdrawing a sample of the liquid at intervals, and determining the rubber content by evaporation.

Perhaps of more interest than the rate of passage into solution is the swelling which first takes place, and attention has been directed to this phenomenon, as it has been suggested that the rate of swelling may afford an indication of the value of the rubber for manufacturing purposes.

The velocity of the process of swelling has been investigated by Posnjak,\* employing an apparatus by means of which the increase in volume of the sample could be determined directly as swelling proceeded. Results were obtained for a number of liquids at pressures of one to six atmospheres, and it was found that a definite equilibrium between the swelling liquid and the swollen rubber was established at a given pressure. The liquids varied in their swelling capacity as determined by the percentage taken up by the rubber under similar conditions of temperature and pressure, the following order being derived: carbon tetrachloride, chloroform, tetrachlorethane, toluene, benzene and ethyl ether. By immersing discs of Para rubber in different solvents and determining the increase in weight at intervals until maximum swelling was attained, Spence and Kratz † obtained a somewhat similar order for the same liquids, and noted that both the maximum swelling capacity and the rate of swelling were increased by the presence of more than 1 per cent. of trichloroacetic acid or more than 10 per cent. of acetic acid, although at lower concentrations no effect was produced.

While raw rubber exhibits the phenomenon of swelling before passing into solution, this property is diminished by mastication or by mechanical working of the rubber,‡ as, for example, in the operation of "milling" or mastication between revolving rollers (see p. 200). As mastication proceeds the swelling is less evident when the rubber is immersed in a suitable liquid, and eventually the condition is reached when the rubber passes directly into solution without a preliminary swelling. The effect of mastication is also to render the insoluble portion less apparent when the rubber is dissolved; this is due not to any chemical change having occurred, but rather to the mechanical working having reduced this constituent to an extremely fine state of division, so that only a slight opalescence is observed in the resulting solution.

Not only does raw rubber swell in liquids in which it will ultimately

\* *Koll. Chem. Beihefte*, 1912, 3, 417.

† *Koll. Zeit.*, 1914, 15, 217.

‡ Spence and Kratz, *loc. cit.*

dissolve, but a similar effect is produced by immersing in liquids such as water, alcohol, acetone, etc., although in such cases the process takes place exceedingly slowly and the degree of swelling is much less pronounced than when rubber solvents are employed.

### VISCOSITY OF RUBBER SOLUTIONS

Solutions of raw untreated rubber are characterised by possessing a high degree of viscosity, and it has been suggested \* that there might exist some relationship between the viscosity of such solutions and the mechanical properties of the rubber after vulcanisation. A considerable amount of work has been carried out on the determination of viscosity, firstly by Axelrod (*loc. cit.*), who investigated the behaviour of concentrated solutions, employing a simple type of apparatus which, however, did not admit of exact determinations being made. Schidrowitz and Goldsborough (*loc. cit.*) later showed that by working with dilute solutions in the neighbourhood of 1 per cent. and using an Ostwald viscometer, the experimental conditions could be controlled so as to give a high degree of accuracy. The rubber was dissolved in benzene, the solution filtered through glass wool to remove mechanical impurities, and the time of flow through the capillary at a standard temperature determined. The concentration was ascertained by evaporating a measured volume of the solution *in vacuo*, and curves were obtained by plotting concentration against time of flow relative to that of benzene through the same viscometer. By working with solutions of three different concentrations, approximately 0.25 per cent., 0.5 per cent. and 1.0 per cent., it was found that the viscosity-concentration curves became very steep below 1 per cent. and were then apparently linear. By taking two separate points on this linear portion the viscosity of a hypothetical 100 per cent. solution, *i. e.* pure rubber, could be calculated. From further consideration of a number of curves Schidrowitz † concluded that they could not be adequately expressed by the linear equation, and suggested instead that a tangent should be drawn at a definite point on the curve, for example, 1 per cent. concentration, and from the tangent of the angle which this made with the abscissa axis the viscosity of a 100 per cent. solution could be calculated according to the scale employed.

Various methods of expressing the results of viscosity determinations have since been proposed, Fol, for example, ‡ employing for purposes of comparison the area enclosed by the viscosity curve, the co-ordinate axes, and

\* *E. g.* Axelrod, *Gummi Zeit.*, 1905, 19, 1053; 20, 105; Schidrowitz and Goldsborough, *J. S. C. I.*, 1909, 28, 3.

† *Rubber*, Methuen, London, 1911, p. 161.

‡ *I. R. J.*, 1913, 45, 679.

the ordinate at 1 per cent. concentration, which value he designates the "viscosity number." The method was simplified by Van Rossem,\* who noted, in comparing the results of over 500 determinations, that the curves did not intersect; all curves passing through a given point at a particular concentration will therefore follow the same course and hence enclose the same area. Instead of constructing the curve from the results of a number of readings, it is therefore necessary simply to take the relative viscosity of a solution of as high a concentration as can conveniently be employed, namely, 1 per cent., from which the viscosity curve and hence the viscosity number may be deduced.

Gorter † proposed the use of the "viscosity index," which is the logarithm of the relative viscosity (benzene = 1) of a solution of 1 gram of rubber in 100 c.c. benzene, a value which has been adopted by several workers, although Van Rossem (*loc. cit.*) has pointed out that it does not possess any advantage over the "viscosity number."

In cases where it is necessary to quote values for viscosity to allow of their being compared *inter se*, the time of flow of a definite volume of solution through the same viscometer is frequently regarded as sufficient, although under these circumstances it is not possible to correlate the figures with other published data.

The question of determining and expressing viscosity has been thoroughly investigated by a number of Dutch workers, who have agreed upon a uniform procedure to be adopted in regard to experimental methods and expression of results.‡ It has been decided that in all cases the value shall be given as the relative viscosity at 30° C., benzene being taken as unity, of a 1 per cent. solution by weight of the rubber in benzene. The solution is to be made up to correspond as nearly as possible with 1 per cent., and the concentration determined by evaporation of an aliquot portion. By means of a chart which is given the viscosity equivalent to a 1 per cent. solution may be read off.

A good deal of work has been published on the technique of viscosity determinations, as, in common with other colloids, the behaviour of rubber solutions depends to a great extent on the previous history of the sample and on the method of preparing the solutions. In the case of rubber the difficulty of obtaining a clear solution is at once encountered, owing to the presence of the insoluble constituent. This may seriously interfere with the passage of the solution through the capillary, and for this reason it has been

\* *Delft Comm.*, 3, 81.

† *Mededeelingen over Rubber*, No. IV, Buitenzorg, 1915.

‡ *Archief*, 1920, 4, 132.

recommended that the solutions should be filtered through glass wool before carrying out the determinations.

It has been objected that filtration of the insoluble particles may lead to a fictitious value for the viscosity, principally because there is a possibility of rubber being retained which may have a different viscosity from that which is dissolved. Both Fol (*loc. cit.*) and Stevens \* have shown that by fractionally dissolving rubber in benzene the fraction which goes into solution first possesses a lower viscosity than the fractions subsequently dissolved, but this may be explained by the influence of the resins which are present in the first fractions and which will tend to give lower values. If as much as possible of the rubber is dissolved, say 90 per cent., there is little likelihood of the results being adversely affected.†

During the preparation of the solutions and the subsequent manipulations it is important that light be excluded, otherwise a marked reduction in viscosity takes place. This effect was originally attributed by Fol to the shaking necessary in order to bring the rubber into solution, and to repeated passages through the capillary of the viscometer, but Van Rossem (*loc. cit.*) showed that neither of these factors could be held responsible for the changes observed, as these did not occur if the operations were conducted in the dark. The effect of light has been investigated by several workers,‡ who have shown that even in diffused daylight the change is very pronounced. By exposure to ultra-violet rays the action is greatly accelerated. Bernstein § having in this way succeeded in reducing the viscosity of a 3 per cent. solution of Para rubber from 180 to 15 units in one hour. Under certain conditions, however, exposure to light may produce the reverse effect, Porritt || having cited an instance in which a solution of previously masticated rubber, sealed in a glass tube with rigid exclusion of air, suddenly set to a gel on exposure to ordinary daylight; on admitting air, however, liquefaction took place rapidly.

This reduction in viscosity is observed when the solutions are heated in contact with inert gases such as hydrogen, nitrogen and carbon dioxide, but is greatly accelerated by air or oxygen even though oxidation does not take place.

The effect of heating rubber solutions is similar to that of exposure to light, a reduction in viscosity occurring although a preliminary increase is sometimes noted.¶

The influence of traces of acid, such as chloracetic acid, which cause a

\* *J. R. J.*, 1913, **46**, 345.

† Fol, *loc. cit.*, Van Heurn, *Delft Comm.*, **3**, 86.

|| *J. R. J.*, 1920, **60**, 1161.

† Van Rossem, *Delft Comm.*, **3**, 90.

§ *Koll. Zeit.*, 1913, **12**, 194.

¶ Schidrowitz, *Rubber*, p. 161.



marked reduction of viscosity in rubber solutions has already been referred to (p. 52).

#### VALUE OF VISCOSITY TESTS

Although the experiments of Schidrowitz and Goldsborough (*loc. cit.*) and of Van Heurn \* indicated that for the same species of rubber a high solution viscosity was correlated with good tensile properties in the raw rubber, further work has shown that the same relation does not always hold after the rubber has been vulcanised.† The whole question has been reviewed very thoroughly by De Vries,‡ who has examined the results obtained with a considerable number of samples of rubber prepared in a variety of ways. Thus on fractionally coagulating latex it was found that while the first clot possessed a higher solution viscosity as compared with that obtained by completing the coagulation, the tensile properties after vulcanisation were inferior. Similarly, treatment with formaldehyde gave a rubber having tensile properties equal to the untreated sample although the viscosity was lower. De Vries concludes that there are several factors which contribute to a low viscosity concurrently with inferior tensile properties, although it is equally true that other factors may conduce to low viscosity with normal tensile and vulcanising properties. Unless the previous history of a sample is known, therefore, the results of viscosity determinations cannot be applied in the evaluation of raw rubber with any degree of certainty.

#### ACTION OF HEAT ON RUBBER

When heated in air rubber softens and becomes sticky or "tacky" at a temperature of 160° C., and melts in the neighbourhood of 220° C., but these temperatures cannot be stated with precision, as the effect of heating at a comparatively low temperature for a long time may be similar to that of heating at a higher temperature for a shorter time. It was observed by Gladstone and Hibbert § that, after heating, rubber was less readily dissolved than before, but Van Heurn || has shown that this is the case only when the rubber is in contact with an inert gas, such as carbon dioxide, heating under these conditions at 130° C. for four hours causing a considerable proportion of the rubber to resist the action of solvents. On the other hand, heating in contact with air does not affect the solubility of the rubber.

In both cases, however, Van Heurn found a marked reduction in the viscosity of the solutions obtained after the rubber had been heated as

\* *Delft Comm.*, 3, 98.

† *Archief.*, 1918, 481.

‡ *Delft Comm.*, 4, 116.

† Van Heurn, *loc. cit.*

§ *J. C. S.*, 1888, 680.

compared with those prepared from the unheated sample. As in the case of solutions of rubber, the effect of heat in reducing the viscosity is less marked, although not entirely negligible, in absence of oxygen.\* Heating below 70° C., unless continued for many hours, produces little effect whether air is present or not. It may also be noted that "tackiness" is not developed to an appreciable extent if the heating be conducted in an inert atmosphere, an observation which was made earlier by Gladstone and Hibbert (*loc. cit.*).

### EFFECT OF LIGHT

The extent to which the viscosity of rubber solutions is affected by exposure to light has already been noted; that this effect may be eliminated by interposing a suitable colour screen,† or even by introducing a soluble dyestuff in the rubber solution itself,‡ has been shown by several workers.

The nature of the absorption of light by rubber was examined by Henri (*loc. cit.*), who found that for wave lengths above 3125 units there was little absorption, and similar results were obtained by Lewis and Porritt,§ who found slight absorption only for wave lengths above 2700 units.

The effect of light rich in ultra-violet, such as is emitted from a mercury vapour lamp, was investigated by V. Henri,|| who exposed films of rubber at a distance of 20 cm. from the source of light. It was noticed that after twenty hours there was a marked change in the appearance of the film, the surface of which showed signs of cracking on being stretched; the exposed samples when dissolved in benzene gave solutions of lower viscosity than the unexposed material. As the film after exposure dissolved to a considerable extent in alcohol, it was concluded that oxidation had occurred. It was then found that after sealing up samples in a quartz glass tube and evacuating, exposure to light was not accompanied by the marked alteration which was noticeable in the presence of oxygen. It appeared, therefore, that the deterioration exhibited by the rubber under the influence of light was due to oxidation stimulated by the actinic rays.

### "TACKINESS"

The phenomenon has been investigated by several workers primarily with the view of elucidating the cause of "tackiness" encountered in certain kinds of raw rubber. This defect, which was more prominently associated with

\* Van Rossem, *Rubber Industry*, 1914, 151; Asano, *Le Caout. et la G. P.*, 1922, 11, 11193.

† Fol, *I. R. J.*, 1913, 45, 631.

‡ Wheatley and North British Rubber Co., E.P. 5915, 1915; Porritt, *I. R. J.*, 1920, 60, 1159; cf. also V. Henri, *Le Caout. et la G. P.*, 1910, 7, 4371.

§ *J. S. C. I.*, 1921, 40, 18 T.

|| *Le Caout. et la G. P.*, 1910, 7, 4371.

certain African rubbers and with the "deresinised" rubbers dealt with in the days before the advent of the plantation product, is characterised by imparting to the surface of the rubber a stickiness or tackiness which in extreme cases affects the material to such an extent that a sheet of rubber may coalesce into a viscous semi-liquid mass. It may be said at once that at the present time its occurrence is comparatively rare. While Henri's work was initiated more to determine the deleterious effect of exposure to air and light, experiments on somewhat similar lines by Fickendey\* were directed more particularly to the specific phenomenon of tackiness. Here again it was found that on exposing to bright sunlight samples of raw rubber in sealed tubes in contact with various gases, only in the tubes containing air or oxygen did tackiness develop. Similar results were obtained by Gorter,† who noted that a very small percentage of oxygen was sufficient to induce tackiness; the experiments in this case were carried out with a rubber known to exhibit a tendency to develop tackiness. As sterilised samples behaved similarly, it was concluded that enzyme action was not responsible for the defect, but that it was due to a process of oxidation. It was shown that in the initial stages oxidation proceeds slowly, and this was held to indicate that the process was one of autoxidation (see p. 87).

Spence‡ had previously expressed the opinion that tackiness was a change due to an alteration either in the physical state of aggregation of the caoutchouc or in the degree of chemical polymerisation, his conclusions being based on the results of experiments in which tackiness was induced by keeping rubber latex in contact with sulphuric acid before coagulating. The tacky rubber thus obtained did not differ in elementary chemical composition from rubber prepared normally from the same latex, but the solution viscosity was much lower than that of the normal sample. Similar views have been expounded by Whitby,§ who regards the actual development of tackiness to be due to "disaggregation" of the rubber, oxidation being a secondary process. As a matter of fact, the progress of oxidation is marked by the gradual disappearance of the tacky nature of the surface, a resinous coating being formed. The theory that tackiness is not primarily due to oxidation receives support from the experiments of Van Rossem,|| who examined the behaviour of rubber on heating to 130° C. in various gases. In this case the changes in properties of the rubber were determined by the solution viscosity and not by the superficial appearance. On heating in oxygen it was noticed that although dis-

\* *Koll. Zeit.*, 1911, **9**, 81.

† *Koll. Zeit.*, 1909, **4**, 70.

|| *Rubber Industry*, 1914, p. 149.

† *Le Caout. et la G. P.*, 1915, **12**, 8724.

§ *I. R. J.*, 1913, **45**, 1043.

aggregation as evidenced by the fall in viscosity took place rapidly, absorption of oxygen did not occur until a definite viscosity, which he called the "critical viscosity," was attained. Comparing the effect of heating in oxygen with that noted in the case of inert gases, it was shown that even in the initial stages the oxygen acted catalytically in hastening the reduction of the solution viscosity and presumably also the disaggregation.

### EFFECT OF MECHANICAL WORKING

One of the first operations incidental to the manufacture of articles from raw rubber is that known as milling, in which the rubber is submitted to a process of mastication or grinding between two steel rollers revolving at uneven speeds. The obvious effect of such treatment is to deprive the rubber of much of its original tensile properties, so that when a strip is pulled it shows little tendency to return to its original position after the tension is released and is indeed easily broken. A further effect of this treatment was revealed by a study of the viscosity of solutions of the rubber made by Boutaric,\* whose experiments showed that as mastication proceeded the solution viscosity of the rubber diminished. This phenomenon was virtually discovered in 1823 by Hancock,† who noted that masticated rubber required less than one-half the proportion of solvent which was necessary when using raw rubber to make a solution which was workable; in other words, Hancock found that the viscosity of a solution of masticated rubber of a certain concentration was no greater than that of a solution of raw rubber of only one-half the concentration.

These results have been confirmed by various workers,‡ and it has been suggested § that determination of the viscosity of a solution of the rubber could be utilised as a means of controlling the operation of milling in the factory.

This change which rubber undergoes on heating or on mastication, and which is characterised by the diminution of the solution viscosity, is frequently referred to as "depolymerisation," but the objection has been raised || that this term is not strictly accurate, as the change is not a chemical one involving a reduction in the size of the molecule, but is rather of a physical nature due to a reduction in the state of aggregation; for this reason Whitby has proposed the term "disaggregation."

Not only does the passage between dry rollers, which is usually accompanied by heating of the rubber, affect the solution viscosity, but a reduction, although

\* *Le Caout. et la G. P.*, 1911, 8, 4965.

† Hancock, p. 11.

‡ *E. g.* Bernstein, *Koll. Zeit.*, 1913, 12, 194; Fol, *Delft Comm.*, 4, 113; Porritt, *I. R. J.*, 1920, 60, 1161.

§ Takeuchi, *J. S. C. I.*, 1918, 37, 313 A.

|| Whitby, *I. R. J.*, 1913, 45, 1043.

less marked, takes place during the passage through rollers upon which a stream of water is kept running, as in the washing or crêping of rubber,\* on the plantation or in the factory.

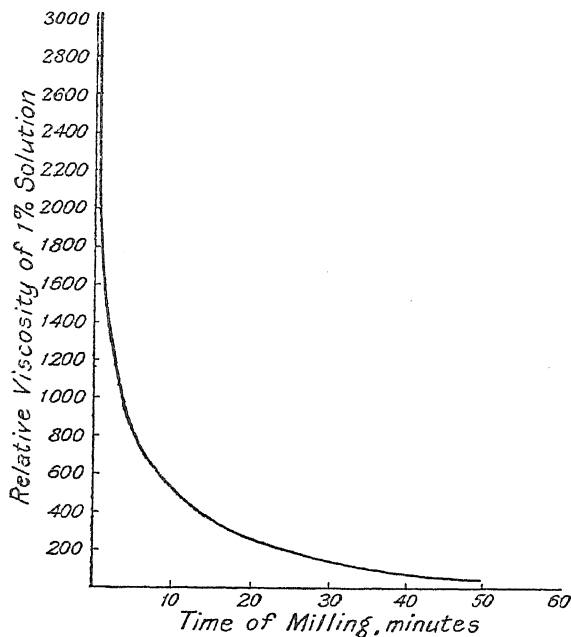


FIG. 1.

The effect of milling is illustrated in Fig. 1, and it will be noticed that the viscosity reduction is very pronounced in the early stages of the process.

If the milling has not been too prolonged the solution viscosity tends to increase on storing the rubber,† although such increase is rarely of great magnitude; the regain is favoured by keeping in a comparatively warm place.

\* Van Heurn, *Delft Comm.*, 4, 113.

† *Ibid.*, 4, 118.

## CHAPTER VII

### CHEMICAL PROPERTIES, CONSTITUTION AND SYNTHESIS

VARIOUS methods have been described for preparing caoutchouc in a pure state from the naturally occurring rubber. As a typical example may be cited that recommended by Heim and Marquis,\* in which the raw material is first washed with water, then extracted with acetone, after which it is dissolved in benzene, the solution filtered and the caoutchouc precipitated by addition of acetone or alcohol. Such purified material gives on analysis figures closely agreeing with the empirical formula  $C_5H_8$ ; earlier analyses made by Faraday, Ure and Greville Williams gave results which showed some divergence from this formula, although it may be noted that in each case the hydrocarbon nature of the caoutchouc was emphasised. It has frequently been stated † that even in a purified caoutchouc there is present a substance containing oxygen, although it has not been regarded as essentially a constituent of the caoutchouc. The view which is almost universally accepted at present is that caoutchouc, the material to which rubber owes its characteristic properties, is a hydrocarbon of empirical formula  $C_5H_8$ .

Of the chemical changes which caoutchouc undergoes, perhaps the most interesting historically are those arising from destructive distillation. Among the earlier workers may be mentioned Gregory, Dalton, and Himly, who found that by distillation oily substances could be obtained, and Barnard, who in 1833 ‡ obtained a patent for "a solvent not hitherto used in the arts," which was obtained by distilling rubber from an iron retort, and which was found to dissolve rubber itself. A systematic study of the distillation products was made in 1837 by Appolinaire Bouchardat, § and later by Greville Williams, || who submitted the crude distillate to a process of purification and obtained (1) a liquid boiling at  $37^\circ C$ . which was found to have the formula  $C_5H_8$ , and to which he gave the name "Isoprene"; (2) a large proportion

\* *J. S. C. I.*, 1915, **34**, 1062.

† *E. g.* Weber, *ibid.*, 1900, **19**, 215; Gladstone and Hibbert, *Trans. Chem. Soc.*, 1888, **53**, 679.

‡ E.P. 6466. § *Journal de Pharmacie*, 1837, **23**, 457. || *Proc. Roy. Soc.*, 1860, **10**, 516.

of a hydrocarbon boiling at  $170^{\circ}\text{C}$ .— $173^{\circ}\text{C}$ . having a molecular formula  $\text{C}_{10}\text{H}_{16}$ , identical with the "caoutchine" of Himly; (3) a fraction boiling above  $300^{\circ}\text{C}$ . to which the name "Heveene," already used by Bouchardat, was given. The "caoutchine" fraction has since been shown to consist of dipentene.

Other products isolated by Gustave, son of A. Bouchardat,\* were butylene, ethylene and methane; later trimethylethylene was found in the isoprene fractions by Ipatiew and Wittorf. As some of these are produced only in small proportion, there is a possibility that they result from the decomposition of resinous or other constituents of the natural rubber.

An idea of the proportions of the various fractions may be gathered from the experiments of Weber,† who obtained the following, expressed as percentages of the rubber taken :

Isoprene	.	.	.	.	.	6.2 per cent.
Dipentene	.	.	.	.	.	46.0 " "
Heveene	.	.	.	.	.	17.0 " "
Polyterpenes	.	.	.	.	.	26.8 " "
Carbon Residue	.	.	.	.	.	1.9 " "
Mineral Residue	.	.	.	.	.	0.5 " "
Loss (water and gases)	.	.	.	.	.	1.4 " "

#### SYNTHETIC FORMATION OF CAOUTCHOUC

Continuing his work on the products of distillation, G. Bouchardat examined particularly the isoprene fraction and noted that when heated at  $280^{\circ}\text{C}$ . in a sealed tube in presence of carbon dioxide, polymerisation occurred with formation of a viscous mass containing a substance having the formula  $\text{C}_{10}\text{H}_{16}$ , now known as dipentene, and a high boiling solid which he called colophene, and which probably contained caoutchouc.‡ Later, in 1879, he found that polymerisation could be induced more readily by shaking with concentrated aqueous hydrochloric acid, in this case the reaction product yielding, after distilling off unchanged isoprene, a solid mass of which he wrote that "it possesses the elasticity and other properties of rubber itself. It is insoluble in alcohol, swells up in ether, and also in carbon disulphide, in which it dissolves after the fashion of natural rubber." The only means of characterising the material other than by its appearance was by noting that it yielded the same substances on destructive distillation as did the natural product.§ The subsequent work of Tilden || afforded confirmation of this observation, as a similar polymerisation was noted in an experiment in which isoprene was treated with nitrosyl chloride.

\* *Bull. Soc. Chim.*, 1875, **24**, 108.

† *Compt. rend.*, 1879, **89**, 361.

|| *Chem. News*, 1882, **46**, 120.

† *Chemistry of India Rubber*, p. 29.

§ *Ibid.*, 1879, **89**, 1117.

Wallach afterwards found \* that isoprene underwent polymerisation on keeping in sealed tubes exposed to light, and Tilden † drew attention to this phenomenon, at the same time noting that the product could be vulcanised with sulphur in the usual way, thus further emphasising the similarity of the material to natural rubber. It is of interest to note that Tilden had obtained his isoprene from turpentine by passing the vapours through a hot tube, and in this respect a distinct advance had been made towards a possible commercial synthesis of rubber, as in previous cases the isoprene had been obtained by the distillation of rubber itself.

Further instances of autopolymerisation have since been recorded by Weber, ‡ and by Pickles. § In the latter instance the isoprene had been kept in the dark for upwards of three years, and even then polymerisation was not complete, as the caoutchouc was obtained as a solid mass only after pouring the viscous liquid into alcohol, which dissolved out the intermediate polymers. Pickles was able to characterise the material by preparing the derivatives formed by the action of bromine and nitrogen trioxide, in each case obtaining products similar to those given by natural rubber.

From the foregoing it will be seen how the conviction first expressed by Bouchardat, that rubber was in fact a polymer of isoprene, steadily gained ground; the chemical individual present in rubber and conferring on it the characteristic properties came to be called "polyprene," a name which is still frequently employed to this day.

### CONSTITUTION OF ISOPRENE

The elucidation of the structure of the caoutchouc molecule demanded in the first place a knowledge of the constitution of isoprene.

The work of Greville Williams and G. Bouchardat established the empirical formula  $C_5H_8$ , and Tilden || suggested that the constitution was that of a  $\beta$ -methylbutadiene,  $CH_2 \cdot C(CH_3) \cdot CH : CH_2$ , although no experimental evidence was brought forward in support of this contention. The correctness of Tilden's view was proved by the syntheses accomplished by Kondakow, ¶ Ipatiew and Wittorf, \*\* and Euler. ††

Perhaps the most conclusive proof is afforded by the synthesis of Euler, who employed a method similar to that worked out by Ciamician and Magnaghi ‡‡ for the preparation of erythrene. Starting with  $\beta$ -methyl pyrrolidine, the

\* *Annalen*, 1887, **238**, 88.

† *J. S. C. I.*, 1894, **13**, 11.

‡ *Chem. News*, 1882, **46**, 129.

\*\* *J. prakt. Chem.*, 1897, **55**, 1; Ipatiew, *ibid.*, 4.

‡‡ *Gazz. Chim. Ital.*, 1895, **15**, 485.

† *Chem. News*, 1892, **65**, 265.

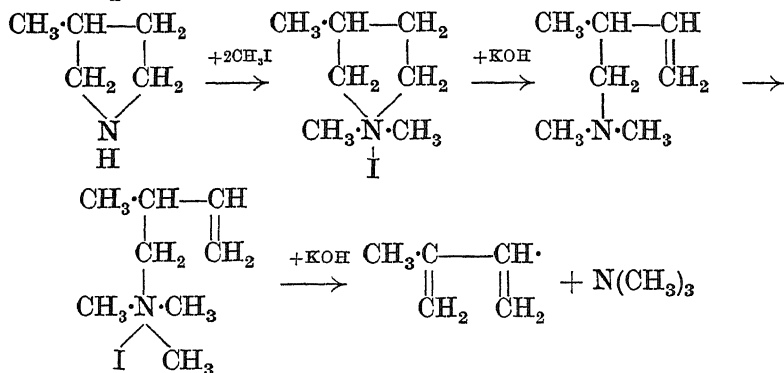
§ *Trans. Chem. Soc.*, 1910, **97**, 1085.

¶ *J. Russ. Chem. Soc.*, 1888, **20**, 706; 1889, **21**, 39.

†† *Ber.*, 1897, **30**, 1989.



methiodide was first formed and hydrogen iodide eliminated to give a base, which was in turn converted into the methiodide; this on removal of hydrogen iodide yielded isoprene.

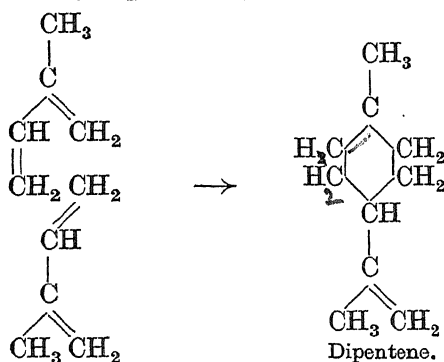


### CONSTITUTION OF CAOUTCHOUC

The structure of isoprene having thus been established and proof obtained that caoutchouc was itself a polymer of isoprene, the manner in which this polymerisation occurred still remained to be determined.

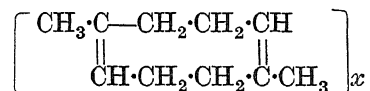
The addition of bromine was known to result in the formation of a derivative, the so-called tetrabromide,  $\text{C}_{10}\text{H}_{16}\text{Br}_4$ , indicating the presence of one double bond for each  $\text{C}_5\text{H}_8$  in the molecule. The tetrabromide, however, afforded no clue to the structure of the parent hydrocarbon owing to its ill-defined character, and for some time the only known degradation product of known constitution was isoprene itself.

Dipentene was, of course, known to be present among the products of destructive distillation of rubber, but its occurrence was held to be due to polymerisation of isoprene originally formed, Bouchardat having already shown that dipentene could be obtained by heating isoprene in a sealed tube. The mode of formation is readily explained by a simple union of two isoprene nuclei.



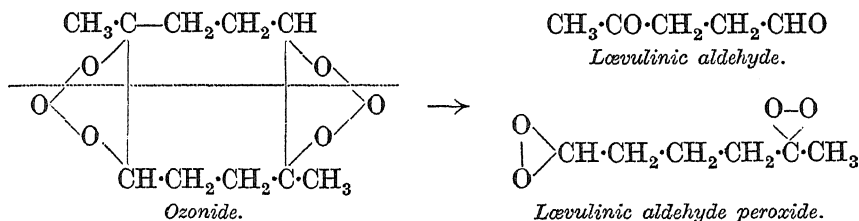
Thus, although dipentene is the chief product of the destructive distillation of caoutchouc, its formation has always been regarded as a secondary process, and the presence in the caoutchouc molecule of a grouping similar to that of dipentene has not been considered likely. Opinion on this point has doubtless been influenced by the fact that whereas caoutchouc may result from the polymerisation of isoprene,  $C_5H_8$ , there is no recorded instance of its preparation from a hydrocarbon of molecular formula  $C_{10}H_{16}$ .

Further important evidence regarding the constitution of caoutchouc was forthcoming from the work of Harries on its reaction with ozone. By passing ozone into a solution of caoutchouc in chloroform there was formed an ozonide which on evaporation of the solvent was obtained as a vitreous mass. After purification, by solution in ethyl acetate and precipitation with petroleum spirit, it was found to have the composition  $(C_{10}H_{16}O_6)_x$ , that is to say, two ozone residues are taken up for every  $C_{10}H_{16}$ , further evidence of the presence of one double bond for every  $C_5H_8$  in the molecule.\* When heated with water it was found to undergo hydrolysis with formation of lævulinic acid and lævulinic aldehyde, together with small proportions of lævulinic aldehyde peroxide; no other decomposition products could be detected.† The molecular weight of the ozonide was afterwards found to correspond with the formula  $C_{10}H_{16}O_6$ , and not with that of a polymer, as had previously been supposed. From these experiments Harries concluded that the structure of caoutchouc was that of a closed-chain hydrocarbon of the formula



that is to say, a polymerised dimethylcyclo-octadiene.

The formation of the ozonide and of lævulinic aldehyde and its peroxide as decomposition products was supposed to take place as follows :



lævulinic acid being regarded as a secondary product of the reaction.

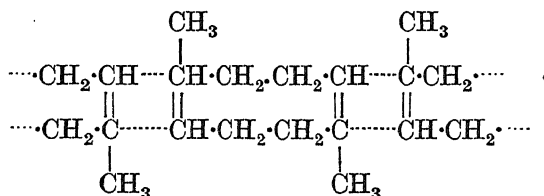
It is of interest to note that at the time the existence in nature of compounds having the  $C_8$ -ring was unknown, but shortly afterwards a derivative of this

\* Ber., 1904, 37, 2708.

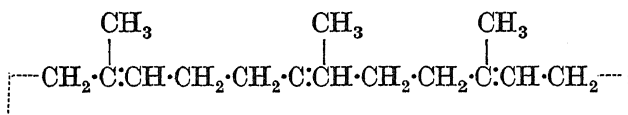
† Ibid., 1905, 38, 1195.

character was obtained by Willstätter from an alkaloid present in the pomegranate. The same worker prepared the parent hydrocarbon 1:5-*cyclo*-octadiene, but all attempts by Harries to reduce caoutchouc ozonide to the dimethyl*cyclo*-octadiene failed, neither did he succeed in obtaining it by any other method.

There were several reasons advanced by various workers to show that the closed-chain formula propounded by Harries could not be finally accepted. In some respects, indeed, it appeared to be in conformity with the behaviour of caoutchouc; for example, the nature of the decomposition products of the ozonides and the formation of isoprene on destructive distillation would be satisfactorily explained. On the other hand, although the formation of a tetrabromide would be expected from a single molecule of dimethyl*cyclo*-octadiene, chemical polymerisation would involve the elimination of double bonds and thus reduce the state of unsaturation. This, Harries explained, could be accounted for by assuming the polymerisation to take place through partial valencies according to Thiele's theory, the unsaturated character of the molecule remaining.



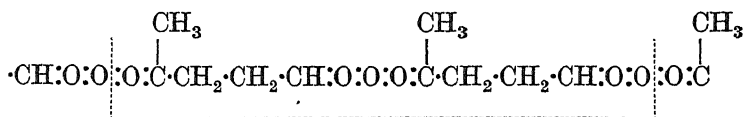
Harries supposed that this loose combination would be easily depolymerised by ozone forming separate  $\text{C}_{10}\text{H}_{16}$  molecules to which ozone would be attached at the point of disruption. As was pointed out by Pickles,\* there was no reason why other reagents such as bromine, which was known to form a tetrabromide of the empirical formula  $\text{C}_{10}\text{H}_{16}\text{Br}_4$ , should not effect a similar depolymerisation; as a matter of fact the tetrabromide exhibits a general behaviour which suggests a body of as complex a character as caoutchouc itself. Pickles postulated a structure represented by the following :



that is to say, a closed chain of  $(\text{C}_5\text{H}_8)$  nuclei, indeterminate in number. The polymerisation in this case is a purely chemical one, the union of the  $\text{C}_5\text{H}_8$  groups being accompanied by a rearrangement of the double bonds. The

\* *Trans. Chem. Soc.*, 1910, 97, 1089.

formation of the ozonide is assumed to take place by a separation of the carbon atoms at the double bonds, as, for example,



The action of water being to bring about fission at the points shown, giving  $\text{C}_{10}\text{H}_{16}\text{O}_6$  units which would yield lævulinic aldehyde, lævulinic aldehyde peroxide and lævulinic acid. Harries himself subsequently abandoned the  $\text{C}_8$ -ring formula as in further experiments,\* he isolated derivatives having a higher number of carbon atoms in the molecule. Starting from Para rubber, the addition product with hydrogen chloride was first prepared; this was heated with pyridine to remove the elements of hydrogen chloride and so regenerate caoutchouc (see p. 83). The ozonide prepared from this yielded on hydrolysis lævulinic aldehyde, a heptane dione, undecanetrione, penta-decanetetraone, lævulinic acid, succinic acid (in some instances), hydrochelidonic acid, methylcyclohexanone, acetic acid and a number of unidentified products. The presence of the triketone and the tetraketone is explicable only by assuming a larger ring than the octadiene. Further, it was shown that the molecular weight of the ozonide in benzene solution was 535, corresponding to  $(\text{C}_5\text{H}_8\text{O}_3)_5$ , the theoretical value for which is 580, and on these grounds it was assumed that the caoutchouc molecule was formed by the union of five  $\text{C}_5\text{H}_8$  nuclei to form a 20-carbon atom ring. Olivier, however, has objected † that the molecular weight of the ozonide cannot be taken as a criterion, since he has been unable to obtain constant values, considerable variations being observed according to the method of treating with ozone.

Later experiments ‡ have led Harries to the conclusion that there are more than five isoprene nuclei present, as, if the dihydrochloride formed by the addition of hydrogen chloride to caoutchouc is reduced by means of zinc dust, a hydrocaoutchouc,  $\text{C}_{35}\text{H}_{62}$  or  $\text{C}_{40}\text{H}_{70}$ , is formed which may be distilled unchanged. The compositions of the ozonide and of the bromide afford further evidence of the existence of thirty-five or forty carbon atoms in the molecule, pointing to the presence of at least seven or eight  $\text{C}_5\text{H}_8$  nuclei.

Thus Harries has finally adopted the formula originally put forward by Pickles, who himself suggested that at least eight isoprene nuclei were joined to form the closed chain.

Recent work on the hydrogenation of caoutchouc in presence of catalysts

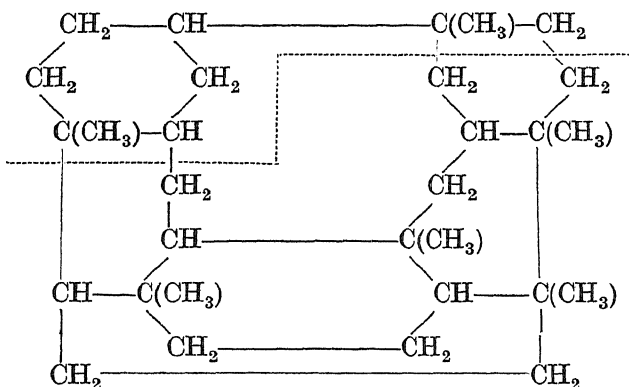
\* Harries and Fonrobert, *Annalen*, 1914, **406**, 173. † *Rec. Trav. Chim.*, 1921, **40**, 665.

‡ Harries and Evers, *Chem. Zentral.*, 1921, **92**, 111, 1358.

(see p. 85) lends support to the view that the molecule must contain a comparatively large number of carbon atoms.

An entirely different theory regarding the structure of the caoutchouc molecule has recently been propounded by Boswell,\* who has sought to explain the production of terpenic substances, such as dipentene, on submitting caoutchouc to destructive distillation, and dinitrohydrocuminic acid, on heating with nitric acid (see p. 84).

Caoutchouc is regarded as having the molecular formula  $C_{30}H_{48}$  represented by the following constitution :



On examination it will be seen that the structure corresponds to a compound formed by the union of five isoprene nuclei, and in this respect is in accordance with known facts.

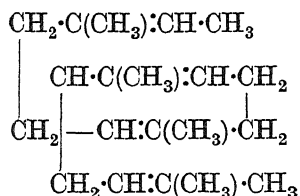
It is also easy to understand the formation of dipentene, as indicated by the dotted line, and of isoprene on destructive distillation. At the same time a number of other hydrocarbons, for example, dimethylbutadiene, should be produced by simple fission, and it would be interesting to examine more thoroughly the products of destructive distillation of rubber in the light of the possibilities revealed by the proposed formula, as hitherto the higher boiling fractions have not been characterised.

There is present one residue capable of reacting as dimethylcyclo-octadiene which would account for the formation of lævulinic aldehyde and lævulinic acid from the ozonide, although not in very considerable proportion, calculated on the rubber taken.

The molecule is represented as completely saturated; on this account the formula does not satisfactorily explain the unsaturated nature of caoutchouc as evidenced by its behaviour towards bromine, which yields a derivative  $(C_{10}H_{16}Br_4)_x$  by simple addition of halogen.

\* I. R. J., 1922, 64, 983.

Among other formulæ which have been proposed may be mentioned those of Barrow \* and Kirchhof,† in which the carbon atoms are supposed to be arranged in a long chain forming a spiral. Kirchhof, in fact, assumes an open-chain structure for caoutchouc present in Para rubber, and regards the molecular formula as  $C_{20}H_{34}$ , instead of being a multiple of  $C_5H_8$ . Caoutchouc present in Congo rubber is, however, supposed to be of the same empirical composition as synthetic caoutchouc from isoprene, *i. e.*  $(C_5H_8)_x$ . The possibility of caoutchouc having a formula other than that represented by a multiple of  $C_5H_8$  is one that has probably been excluded on account of its supposed formation by simple polymerisation of isoprene. For this reason the results of analyses of specially purified samples of caoutchouc have always been taken as affording confirmation of the empirical formula  $C_5H_8$ , even though the figures have shown some slight divergence from the theoretical values corresponding to this formula. Indeed, lack of agreement between the analytical results and the theoretical values might be anticipated, owing to the difficulty of obtaining caoutchouc completely free from the accessory substances which are always present in the naturally occurring material. Kirchhof's conclusion that Para caoutchouc consists of a polymer of  $C_{10}H_{17}$  is valid only if the product of the polymerisation of isoprene is different from the naturally occurring material. While synthetic caoutchouc from isoprene bears a close resemblance to Para rubber in respect to its physical and mechanical properties, the only definite chemical analogy is afforded by the decomposition products of the ozonide. If Para rubber were represented by the formula suggested by Kirch-



hof, the products of destructive distillation would be expected to contain other low-boiling hydrocarbons besides isoprene, although the production of both isoprene and dipentene is possible. The decomposition of the ozonide formed from a compound of this nature should yield products different from those which have hitherto been isolated, although both Olivier and Boswell (*loc. cit.*) have cast doubts on the quantitative formation of an ozonide such as has been postulated by Harries. While the formulæ proposed by Boswell and by Kirchhof differ materially from those which have hitherto found

\* I. R. J., 1911, 41, 1354.

† Koll. Chem. Beihefte, 1922, 16, 47.

acceptance, they may provide a stimulus to further research on the structure of the chemically reacting unit present in natural rubber.

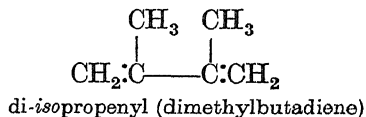
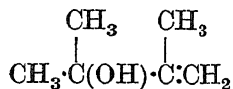
### TECHNICAL SYNTHESIS OF RUBBER

While at first the efforts of chemists were directed towards the synthesis of caoutchouc from the point of view of elucidating its structure, the possibility of realising the synthesis on a commercial scale was one that was not entirely overlooked. Thus in 1882\* Tilden wrote concerning the polymerisation of isoprene: "It is this character of isoprene which gives it a somewhat practical interest, for, if it were possible to obtain this hydrocarbon from some other and more accessible source, the synthetical production of india-rubber could be accomplished."

It was not, however, until about 1909 that the problem of industrialising these earlier discoveries attracted attention. In the meantime it had been observed that not only isoprene but many other unsaturated hydrocarbons were capable of polymerising, giving in some cases elastic bodies.

In 1881, for example, Hofman † noted that piperylene, an isomer of isoprene, having the formula  $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}_2$ , underwent a partial polymerisation during distillation. Tilden in 1884‡ suggested that just as isoprene polymerised to give dipentene, so homologues of isoprene should polymerise to give a series of terpenes.

Marintza § in 1890 obtained an oily polymeride from dimethylisopropenyl carbinol, which he supposed had been formed from the di-isopropenyl first produced by elimination of  $\text{H}_2\text{O}$ .



Couturier || showed that the action of heat on this hydrocarbon produced a resinous mass, and later Kondakow ¶ showed that by heating with alcoholic potash polymerisation took place with formation of a white elastic mass, the properties of which resembled those of rubber. Kondakow \*\* further showed that polymerisation occurred on keeping or on exposure to light, and thus for the first time indicated the possibility of producing rubber-like substances from other hydrocarbons than isoprene.

\* *Chem. News*, 1882, **46**, 120.

† *Trans. Chem. Soc.*, 1884, **45**, 411.

‡ *Ann. Chim. Phys.*, 1892, **26**, 485.

\*\* *Ibid.*, 1901, **64**, 109.

† *Ber.*, 1881, **14**, 665.

§ *Chem. Soc. Abs.*, 1890, **i**, 728.

¶ *J. prakt. Chem.*, 1901, **63**, 113.

Elastic polymers were subsequently prepared by Thiele\* from piperylene, by Klages† from phenylbutadiene, by Kronstein‡ from cyclopentadiene, and by Willstätter§ from cyclo-octadiene.

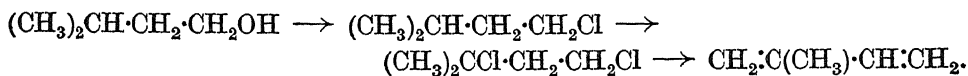
From the composition of the parent substances these polymers could not in all cases be identical with the hydrocarbon present in rubber. This was of comparatively small moment, as it is quite conceivable that there might be obtained from some hydrocarbon other than isoprene products having mechanical properties superior even to those of rubber. The question thus resolved itself into the preparation of isoprene or isomers or homologues thereof, and the discovery of suitable methods of effecting polymerisation.

At that time isoprene was the only hydrocarbon which had been prepared from comparatively abundant raw material, namely, turpentine, and even then the yields obtained were relatively small. Methods of polymerisation were unsatisfactory, as the most effective chemical agent, hydrochloric acid, gave hydrochlorides and other products in addition to caoutchouc; auto-polymerisation, on the other hand, while giving a fairly pure product, was a process which took months or years to complete.

### PREPARATION OF ISOPRENE AND HOMOLOGUES

It is perhaps natural that the first attempts to prepare isoprene on a large scale employed as initial material turpentine, from which Tilden had already obtained the hydrocarbon. A process devised by Heinemann|| consisted in passing the vapours of turpentine over heated finely divided metals, and Harries and Gottlob¶ succeeded in obtaining increased yields by passing the vapour over an electrically heated platinum wire; turpentine as raw material was, however, abandoned at an early stage, as supplies were more likely to become exhausted than were those of rubber.

Other raw materials suggested were starch, the fermentation of which may be controlled so as to give comparatively high yields of *iso*-amyl alcohol. On treating with hydrochloric acid *iso*-amyl chloride is formed, which is then chlorinated to give isomeric dichlorides; these on passing over heated soda lime yield isoprene together with isomeric hydrocarbons : \*\*



The dichlorides may also be prepared by chlorinating the *isopentane* present in Galician petroleum.††

\* *Annalen*, 1901, **319**, 226.

† *Ber.*, 1902, **35**, 2650.

‡ *Ibid.*, 1902, **35**, 4151.

§ *Ibid.*, 1905, **38**, 1975.

|| *E.P.* 14040, 14041, 1910.

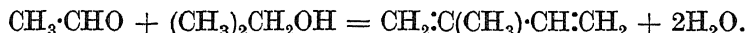
¶ *Annalen*, 1911, **383**, 228.

\*\* *Matthews and Strange*, *E.P.* 4572, 1910.

†† *Ibid.*, 4189, *E.P.* 1910.



By passing a mixture of acetaldehyde and isopropyl alcohol over heated alumina, isoprene is produced, according to Ostromisslenski,\* as follows :



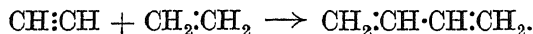
Strange as it may appear at first sight, the efforts of synthesists were directed more to the preparation of homologues of isoprene, of which the most important are :

Erythrene (divinyl or butadiene),  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}:\text{CH}_2$ .

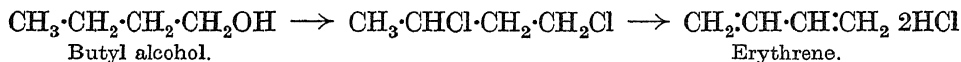
Piperylene ( $\alpha$ -methylbutadiene),  $\text{CH}(\text{CH}_3):\text{CH}\cdot\text{CH}:\text{CH}_2$ .

Di-isopropenyl ( $\beta\gamma$ -dimethylbutadiene or methylisoprene),  
 $\text{CH}_2\cdot\text{C}(\text{CH}_3)\cdot\text{C}(\text{CH}_3):\text{CH}_2$ .

Erythrene was originally obtained by Berthelot,† on passing a mixture of acetylene and ethylene through a red-hot tube :



Methods analogous to those employed for preparing isoprene may also be utilised for the preparation of the lower homologue. If, for example, instead of starting with *iso*-amyl alcohol, butyl alcohol is chlorinated and the dichloride passed over heated soda lime, erythrene is produced :



This preparation is interesting in that a special method of fermentation of starchy materials was developed by Fernbach and Strange,‡ in which considerable proportions of butyl alcohol and acetone were produced. This process, originally elaborated as a step in the production of synthetic rubber, became of considerable importance during the European War in furnishing supplies of acetone and butyl alcohol, both valuable raw materials for other purposes.§

Another method of preparing erythrene is that proposed by Ostromisslenski (*loc. cit.*), in which alcohol vapour together with air is passed over heated copper, whereupon a proportion of acetaldehyde is produced; the mixture of aldehyde and alcohol is then passed over heated alumina, giving the hydrocarbon with elimination of water :



A possible synthesis from coal-tar derivatives is that in which phenol is

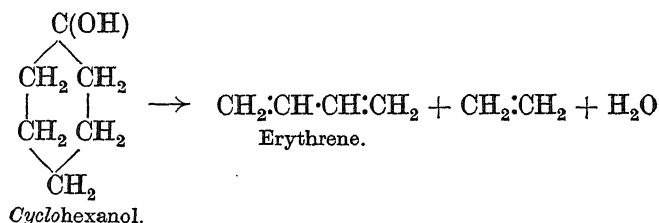
\* *J. Russ. Phys. Chem. Soc.*, 1915, 47, 1472.

† *Annales de Chimie*, 1867, 9, 466.

‡ E.P. 15203, 15204.

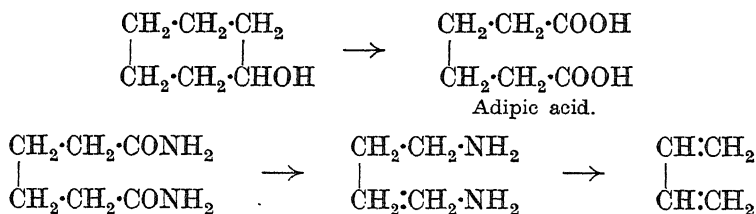
§ For full particulars of the process, see Speakman, *J. S. C. I.*, 1919, 155 T.; Reilly, and others, *Biochem. J.*, 1920, 14, 229.

first converted by means of the Sabatier and Senderens method into *cyclohexanol*, which is then slowly dropped on to a hot surface, giving erythrene together with ethylene and water : \*



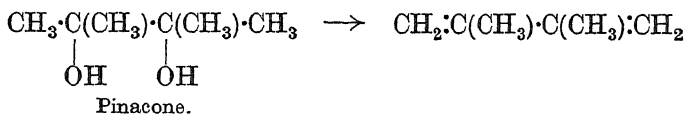
By a similar series of reactions starting from *o*-cresol, which is first reduced to methyl *cyclohexanol*, methyl erythrene (isoprene) may be obtained.

The preparation of erythrene from *cyclohexanol* obtained by reducing phenol may be arrived at by an alternative method, which, however, involves the use of costly materials. In this case the *cyclohexanol* is oxidised to adipic acid, which is then converted into the di-amide. By Hoffmann's reaction this is converted into the di-amine with elimination of two carbonyl groups; exhaustive methylation then yields erythrene :



Starting from *p*-cresol, there is produced methyl adipic acid, which by a similar series of reactions yields isoprene.

Probably the most interesting of all the isoprene homologues is 2:3-dimethyl-butadiene (di-*isopropylene*), which was first prepared by Couturier † by dehydrating pinacone with sulphuric acid :



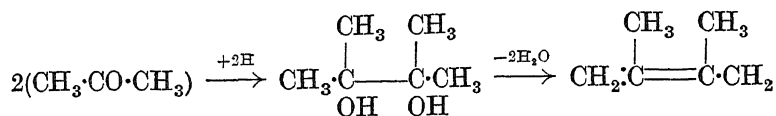
Kondakow ‡ showed that increased yields were obtained by starting with pinacone dihydrochloride, from which dimethylbutadiene resulted on heating with alcoholic potash. Much of the synthetic rubber manufactured in Germany during the War was obtained by polymerising dimethylbutadiene obtained

\* Bayer, Fr. Pat. 425967, 1911.

† Bull. Soc. Chim., 1880, 33, 454.

‡ J. prakt. Chem., 1899, 59, 293.

from pinacone \* by distilling under pressure, during which operation two molecules of water are eliminated. The starting-point in this synthesis was acetylene, which was first converted into acetone, and this was then reduced by means of aluminium and sodium hydroxide to give pinacone : †



The examples cited above represent only a fraction of those which have been proposed for preparing the parent unsaturated hydrocarbons.

No good purpose would be served by enumerating further instances, as in very few cases have these found industrial application; indeed it appears that the preparation of dimethylbutadiene from pinacone was the only method which led to the production of a satisfactory synthetic rubber during the War.

### METHODS OF POLYMERISATION

Although the polymerisation of isoprene to a rubber-like body was established by Bouchardat and by Tilden, and subsequently by other workers, the yields obtained, excepting in cases of autopolymerisation, were unsatisfactory. It was not until 1910 that the problem appeared at last to have been solved by discoveries made almost simultaneously in this country and in Germany. It was, in fact, the application of new polymerising agents, rather than of new sources of unsaturated hydrocarbons, which formed the basis of what was at the time popularly regarded as the discovery of synthetic rubber. In 1908 a group of British chemists, including Prof. W. H. Perkin, Dr. C. Weizmann, Dr. F. E. Matthews and others, were engaged in attempts to elaborate methods for the production of synthetic rubber on an industrial scale. In July 1910 Matthews sealed up a sample of isoprene containing metallic sodium and allowed the tube and contents to remain undisturbed for some time. By September it was noticed that the whole had solidified to a rubber-like mass, ‡ and a patent was applied for on October 25, 1910.§ Thus, even at ordinary temperatures, the change which other workers had found was not complete even after many months, in the presence of sodium proceeded comparatively rapidly.

In the meantime Harries in Germany had been working on the same problem and noticed the polymerising action of sodium, which he described in a paper

\* Staudinger, *Zweitz. Chem. Zeit.*, 1919, **1**, 1-5, etc. † *J. Ind. Eng. Chem.*, 1919, **11**, 819.

‡ See Perkin, *J. S. C. I.*, 1912, **31**, 619.

§ Strange and Graham, E.P. 24790, 1910.

published in June 1911,\* by which time the contents of the British patent had not been disclosed. Thus, although the discovery was first publicly announced by Harries, the British patent application predated this announcement by some months. Harries had previously discovered that on heating isoprene with acetic acid at a little over 100° C. polymerisation occurred.†

Exposure to ultra-violet or X-rays has also been proposed as a method of polymerising isoprene or its homologues.‡

The method which was most favoured in Germany during the War consisted in sealing up the hydrocarbon in metal drums and keeping at a temperature of about 60° C. for four to six months; § the sodium method apparently gave unsatisfactory products, but the polymerisation at ordinary temperatures was somewhat more successful.||

### COMPARISON OF SYNTHETIC AND NATURAL RUBBERS

Owing to its colloidal nature the physico-chemical methods usually adopted for the characterisation of organic substances cannot be applied in the case of caoutchouc. The preparation of characteristic derivatives such as the tetrabromide does not offer a more helpful solution. The examination of the ozonides appeared to Harries to afford the most suitable means of establishing the identity or otherwise of the synthetic with the natural product. In his experiments on polymerisation by sodium and by acetic acid ¶ he prepared a series of caoutchouc-like bodies from the hydrocarbons erythrene, isoprene, and methylisoprene, employing in each case the alternative methods of effecting the condensation. The polymers from erythrene ( $C_4H_6$ ) and dimethylbutadiene ( $C_6H_{10}$ ) could obviously not be identical with natural rubber, a polymer of isoprene ( $C_5H_8$ ). He noted, however, that in all cases the polymerides prepared with the aid of acetic acid behaved differently from those resulting from the action of sodium; to the former he gave the name "normal" rubbers, and to the latter "abnormal" or "sodium" rubbers. It appeared, therefore, that even from isoprene a rubber-like body could be obtained which was not identical with the natural material. A study of the formation and hydrolysis of the ozonides confirmed this opinion, the polymer formed by the aid of acetic acid yielded an ozonide giving the same products and having the same rate of decomposition as the ozonide of natural rubber, whereas the sodium polymer gave an ozonide which did not yield lævulinic aldehyde or acid on decomposition.

\* *Annalen*, 1911, **383**, 188.

† Ostromisslenski, *Fr. Pat.* 442981, 1912.

‡ Gottlob, *I. R. J.* 1919, **58**, 305 *et seq.*

§ *Chem. Zeit.*, 1910, **34**, 315.

§ Norris, *J. Ind. Eng. Chem.*, 1919, **11**, 819.

¶ *Annalen*, 1911, **383**, 157.

Steimmig,\* however, controverted this opinion, and held that even in the "normal" synthetic product there was present a substance formed by the asymmetric polymerisation of isoprene.

At the time when these experiments were carried out the material available was insufficient to furnish data based on actual mechanical tests, which after all must be regarded as the ultimate criteria for the evaluation of synthetic rubber. During the War, however, when stress of circumstances compelled the Central Powers to resort to chemical methods for furnishing supplies of rubber, materials prepared by various processes received a trial. From the parent hydrocarbons, erythrene, isoprene, and dimethylbutadiene, rubbers were produced by cold polymerisation, hot polymerisation, and also by the use of sodium. The best results, as has been noted above, were obtained by the hot polymerisation of dimethylbutadiene, or methylisoprene, and on this account the product was known as methyl rubber.† The cold polymerised methyl rubber was, however, found suitable for making vulcanite articles, and in 1918 as much as thirty tons per month were used in the manufacture of accumulator cells for submarines; in addition, the manufacture of tyres involved the consumption of ten tons per month. This variety was characterised by a lack of adhesive properties and, moreover, could not be dissolved in the usual solvents. For purposes where these properties were specially desirable the hot polymerised material was employed, and such articles as tyre covers, rubber soles, packing sheet and spread fabrics, including those for balloons, were made from this variety. A further synthetic product obtained by polymerisation with sodium in presence of carbon dioxide‡ also found a limited application. All the synthetic rubbers were particularly prone to oxidation and did not resist changes in temperature so well as natural rubber; thus it became necessary to issue instructions to store tyres whenever possible in rooms protected from frost. The methyl rubbers, too, could not be rendered plastic at all readily, and it became necessary to add bodies known as "elasticators" to remedy this defect;§ among compounds which were found useful for this purpose were petroleum and vegetable oils, dimethylaniline, toluidine, and diphenylamine, the last named being specially suitable for rubber used for covering and insulating submarine and other cables.

As a result of the extended trials which the synthetic material has thus received, it appears certain that up to the present the characteristic properties

\* *Ber.*, 1914, **47**, 350.

† For a complete account of the production of synthetic rubber during the War see *I. R. J.*, 1919, **58**, 305, 348, 391, 433.

‡ Cf. Ostromisslenski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1441.

§ *Fr. Pat.* 459, 005, 1913.

of the natural rubber have not been satisfactorily reproduced. Nevertheless, a measure of success has been attained in certain directions, as, for example, in the production of vulcanite or hard rubber, and to a lesser degree in the manufacture of solid tyres (an instance is given in the article cited above of one having run for "many thousand kilometres," but this is quoted as an exceptional case).

Only under the exceptional circumstances occasioned by the blockade, however, was the manufacture resorted to, and with adequate supplies of raw rubber at current prices it is difficult to see how a synthetic process is to succeed. Although it is practically certain that natural rubber is a polymer of isoprene, it is equally certain that the mode of polymerisation and the ultimate degree of polymerisation are important factors which determine the properties of the final product. Until our knowledge of these matters is extended it does not appear to be possible to produce, except it be fortuitously, a synthetic material exactly similar to the natural rubber.

## DERIVATIVES OF CAOUTCHOUC

### ACTION OF HALOGENS

The reactions of caoutchouc with the halogens were studied by Gladstone and Hibbert (*loc. cit.*), who found that on treating chloroform solutions with chlorine in diffused light addition compounds were formed, but that at the same time hydrogen chloride was produced, indicating that substitution was taking place concurrently. The reaction product was eventually obtained as a white powder having the formula  $C_{10}H_{14}Cl_6$ , which corresponded to the addition of six atoms of chlorine and the substitution of two further atoms for two atoms of hydrogen in the parent substance,  $C_{10}H_{16}$ . From a consideration of the optical properties of caoutchouc they had formed the opinion that three double bonds were present for each  $C_{10}H_{16}$  unit in the molecule. The reaction with bromine in dilute solution, however, yielded a white product having the formula  $C_{10}H_{16}Br_4$  and even in presence of excess of the reagent the highest content of bromine obtainable was in the case of the substance  $C_{10}H_{15}Br_5$ , in the formation of which substitution occurred as indicated by the evolution of fumes of hydrogen bromide. No reaction was observed in the case of iodine.

The reaction products with chlorine have been very little studied, probably owing to the difficulty of controlling the reaction so as to avoid substitution, but it may be noted that by working with an ice-cooled benzene solution a less highly chlorinated compound than that obtained by Gladstone and Hibbert is formed \* although from the formula  $C_{10}H_{14}Cl_6$  it is evident that

\* Hinrichsen, Quensell and Kindscher, *Ber.*, 1913, 46, 1283.

substitution occurs. Chlorine derivatives of rubber have been put to industrial use in making acid-resisting varnish, which has been placed on the market under the name of "Duroprene," and it has been proposed to utilise the solid material in the preparation of substitutes for celluloid.\*

The additive compound  $C_{10}H_{16}Br_4$  formed with bromine, and generally described as caoutchouc tetrabromide, has been the subject of numerous researches, as the apparently constant composition of the product formed under definite experimental conditions has led to its being proposed as a means of estimating or characterising the parent hydrocarbon.

If a 1 per cent. solution of bromine in chloroform or carbon tetrachloride is run into a carefully cooled 1 per cent. solution of rubber in the same solvent until bromine is no longer absorbed, and the solution then run into alcohol or acetone, the tetrabromide is precipitated as a white fibrous mass. It is comparatively stable at ordinary temperatures, but on warming hydrogen bromide is evolved, gradually below  $100^\circ C.$ , but more rapidly at somewhat higher temperatures. From the bromide a caoutchouc-like body may be regenerated by heating with alcoholic potassium hydroxide, about half the combined bromine being removed at  $100^\circ C.$ , the remainder only at a higher temperature; † the debrominated material is apparently isomeric, but not identical with the original caoutchouc.

Attempts were made by Weber ‡ to form crystalline derivatives of caoutchouc by the interaction of the tetrabromide with hydroxy-compounds such as phenol; in this way hydrogen bromide was eliminated and an amorphous powder obtained, the analysis of which corresponded closely with the composition  $C_{10}H_{16}(OC_6H_5)_4$ .

Although Gladstone and Hibbert were unable to prepare an iodine derivative, Weber (*loc. cit.*) found that by mixing carbon disulphide solutions of caoutchouc and iodine and allowing to stand for twelve hours, a jelly was obtained which on treating with excess of alcohol yielded a brownish solid insoluble in all ordinary solvents; the analysis agreed closely with that of a compound having the formula  $C_{10}H_{16}I_3$ . Schwartz and Kempf, § however, failed to repeat these experiments and obtained a compound containing only small proportions of iodine; it was noted that on exposure to light iodine was absorbed, but in this case the reaction appears to have been accompanied by oxidation, as they isolated a white powder of a composition corresponding to the formula  $C_{20}H_{27}O_7I$ .

A somewhat similar compound has indeed been prepared by Boswell,

\* Peachey, E.P. 1894/1915.

† J. S. C. I., 1900, 19, 219.

‡ Kirchhof, *Koll. Zeit.*, 1914, 15, 126.

§ Ber., 1913, 46, 1287.

McLaughlin and Parker\* by allowing a carbon tetrachloride solution of caoutchouc, iodine, and hydrogen peroxide, to react in the cold for two weeks. After purification the product was a brownish-yellow resinous mass having the composition  $C_{25}H_{40}O_8I$ .

### ACTION OF HALOGEN ACIDS

By passing moist hydrogen chloride gas into a chloroform solution of caoutchouc and pouring the resulting product into alcohol, Weber (*loc. cit.*) obtained a white flocculent solid which on drying formed a brittle resinous mass having the composition represented by the formula  $C_{10}H_{18}Cl_2$ .

Hydrogen bromide or iodide did not yield analogous compounds, but these have since been described by Hinrichsen, Quensell and Kindscher,† who prepared them by passing the hydrogen halide into a 1 per cent. solution of caoutchouc in benzene cooled in ice. It was found that for every  $C_{10}H_{16}$  two molecules of HBr and one molecule of HI were absorbed, although according to Harries a compound  $C_{10}H_{18}I_2$  may be prepared, which, however, loses one molecule of HI very readily.

From the hydrochloride it is possible to regenerate caoutchouc by heating with piperidine or pyridine in a sealed tube at 125 to 145° C.‡ As in the case of the material regenerated from the tetrabromide, the halogen-free material does not appear to be identical with the original caoutchouc, to which, however, it bears a strong resemblance. This regenerated "caoutchouc" may be again transformed into a hydrochloride and submitted to the same treatment with piperidine, a second regenerate being obtained in which the rubber-like character still persists.§ Even after prolonged boiling in toluene or xylene caoutchouc forms a hydrochloride.

### OXIDES OF NITROGEN

The corrosive action of certain oxides of nitrogen on rubber tubing and stoppers has been recognised for a considerable time, but the systematic study of the reaction was first taken up by Harries.|| In experiments with nitrogen trioxide it was found that the course of the reaction was influenced greatly by the moisture content of the reagents.¶ Thus, on passing very dry nitrogen trioxide into a solution of caoutchouc in dry benzene there was formed a compound which he termed nitrosite "a," having the empirical formula

\* *I. R. J.*, 1922, **64**, 986.

† Harries, *ibid.*, 1913, **46**, 733.

‡ *Ber.*, 1901, **34**, 2991.

§ *Ber.*, 1913, **46**, 1283.

¶ Lichtenburg, *Annalen*, 1914, **406**, 207.

|| *Ibid.*, 1902, **35**, 3256.



$C_{10}H_{16}N_2O_3$ ; it was insoluble in all ordinary solvents and decomposed at 80 to 100° C.

By continued passage of the gas a nitrosite "b" was obtained to which the formula  $C_{20}H_{30}N_6O_{16}$  was assigned; this was soluble in ethyl acetate, acetone and alkalis, was decomposed on heating to 130° C. and reduced Fehling solution.

When moist benzene was employed as solvent and moist  $N_2O_3$  passed in a third compound, nitrosite "c" resulted, the composition of which was in accordance with the formula  $C_{20}H_{30}N_6O_{14}$ ; this was soluble in alkalis and reduced Fehling solution.

Later Harries \* attributed the formation of nitrosite "b" to the action of nitrosyl chloride present in the gas as a result of drying over calcium chloride, but the nitrosite "c" he regarded as a definite compound; the experimental value for the molecular weight was 561, corresponding closely to the formula already assigned to it.

If instead of nitrogen trioxide, the peroxide, obtained by heating lead nitrate, is employed, there is formed, according to Weber,† a nitrosate having the empirical formula  $C_{10}H_{16}N_2O_4$ . Harries‡ and Alexander,§ however, express the opinion that the product obtained by means of nitrogen peroxide corresponds more closely to the nitrosite "c" of Harries.

### NITRIC ACID

If concentrated nitric acid (sp. gr. 1.40) is poured on to dry rubber, a reaction takes place, which is accompanied by rise in temperature, and unless controlled the whole may take fire. A yellowish brittle solid is thus produced which is said to have the composition  $C_{10}H_{12}N_2O_6$ .|| This was found by Ditmar to melt at 142 to 143° C., to be soluble in ethyl acetate, benzaldehyde, and nitrobenzene and to possess the characteristics of a monobasic acid. From subsequent experiments Ditmar concluded that its composition was that of a dinitro-dihydrocuminic acid,  $C_3H_7 \cdot C_6H_4(NO_2)_2 \cdot COOH$ .¶

### SULPHURIC ACID

In recent investigations of the action of concentrated sulphuric acid on solutions of raw rubber in carbon tetrachloride Kirchhof\*\* succeeded in isolating products similar to those resulting from oxidation processes. Thus pale

\* *Ber.*, 1902, 35, 4429.

† *Ibid.*, 1903, 36, 3103.

‡ *Ibid.*, 1905, 38, 87.

§ *Ibid.*, 1905, 38, 181.

|| Ditmar, *ibid.*, 1902, 35, 1401.

¶ *J. S. C. I.*, 1904, 23, 794.

\*\* *Koll. Zeit.*, 1920, 27, 311; 1922, 30, 176.

crêpe treated in this manner yielded 93·5 per cent. of its weight of a brittle powder which on extraction with acetone was separated into a reddish-brown oxidation product, and also a non-oxidised hydrocarbon to which the composition  $C_{10}H_{15}$  is assigned. The prolonged action of concentrated sulphuric acid on a solution of Para rubber in benzene yielded 47·4 per cent. of a reddish-brown acetone-soluble substance having a composition corresponding with the formula  $C_{20}H_{30}O_3$ . By dissolving this in alcoholic potash and acidifying with dilute sulphuric acid a precipitate was formed which, recrystallised from acetone, gave a compound of the same empirical formula melting at 95 to 96° C.; the saponification value was found to be 174 in ethyl alcohol, and 181 in ether solution. The substance reduced Fehling solution and formed a phenyl hydrazone giving crystals soluble in ethyl alcohol, acetone and benzene; this derivative sintered at 90° C. and melted at 120 to 124° C.

### REDUCING AGENTS

By heating caoutchouc at 180° C. with concentrated hydrogen iodide solution Berthelot \* obtained paraffin hydrocarbons boiling above 350° C.

Various attempts have been made to reduce the caoutchouc molecule by direct hydrogenation in presence of catalysts, but only recently has this been successfully attained. Staudinger and Fritsch,† by treatment with hydrogen in presence of platinum at 270° C. at 100 atmospheres pressure, succeeded in obtaining a hydrocaoutchouc having the composition  $(C_5H_{10})_n$ . The substance thus obtained consists of a colourless, inelastic mass which retains the colloidal properties of caoutchouc, and dissolves in benzene, ether and chloroform, but is insoluble in acetone and alcohol. In absence of light, bromine is not absorbed, indicating the saturated character of the hydrocarbon. Although the empirical composition is in accordance with the presence of an unsaturated linking, unless a ring structure is accepted, it is assumed that the molecule is so large that  $C_nH_{2n}$  approximates to  $C_nH_{2n+2}$ .

Hydrogenation under less drastic conditions than those just described has been accomplished by Pummerer and Burkard ‡ employing very dilute solutions of caoutchouc (0·2 to 0·6 per cent.) in presence of spongy platinum as catalyst. Under these circumstances the reaction proceeds at 70 to 80° C. giving hydrocaoutchouc  $(C_5H_{10})_x$ , with properties similar to those of Staudinger and Fritsch's product. Caoutchouc is regarded as consisting of a ring system, or an extremely long open chain of at least twenty isoprene nuclei.

\* *Bull. Soc. Chim.*, 1869, (ii), 11, 33.

† *Helv. Chim. Acta*, 1922, 5, 785.

‡ *Ber.*, 1922, 55, 3458.

## ACTION OF OXIDISING AGENTS

Raw rubber when exposed to the air under normal conditions exhibits little or no tendency to undergo oxidation, although among lower grade varieties this phenomenon is sometimes met with.

This resistance to oxidation, however, is not so marked in the case of rubber which has been submitted to the process of mastication. Thus Spiller \* found that the unvulcanised rubber coating on a piece of fabric after six years had lost its original properties and had become hard and brittle, or "perished," to use the term now applied to such a change. Simultaneously, a proportion of the rubber had become soluble in solvents such as alcohol, and on analysis this soluble portion was found to contain oxygen, the composition corresponding approximately to  $C_{30}H_{48}O_{10}$ ; evidently oxidation had occurred with formation of a hard resinous mass which has since been described as "Spiller's resin." The effect of oxygen was subsequently investigated by Herbst, who passed a current of air for 140 hours through a boiling 1 per cent. solution of purified rubber in benzene. The residue on evaporation showed an increase in weight of approximately 12 per cent., and then consisted of a syrupy mass from which there were separated a clear brownish syrup of composition  $C_{10}H_{16}O$ , soluble in petroleum ether, a pale yellow, friable solid, insoluble in petroleum ether, having the composition  $C_{10}H_{16}O_3$ , and a very small proportion of a hard brittle resin of similar composition. The question was further examined by Peachey,† who exposed thin films of rubber deposited on the inside of a flask to an atmosphere of moist oxygen at 85° C. and determined the absorption of gas volumetrically. When no further reduction in volume of gas occurred it was found that the amount absorbed corresponded to four atomic proportions for every  $C_{10}H_{16}$  unit; the rate of oxidation was shown to be much accelerated by first removing the resins, but the final extent of oxygen absorption was the same whether the rubber contained the naturally occurring resins or whether these were previously extracted. It was subsequently found ‡ that carbon dioxide was a product of oxidation (cf. Perkin, discussion on previous paper) and was present in the residual oxygen to the extent of one atomic proportion for every four  $C_{10}H_{16}$  units; thus the total amount of oxygen interacting was greater than had previously been supposed, although the amount absorbed and remaining combined with the rubber was the same as indicated by the reduction in volume, since the carbon dioxide formed replaces an equal volume of oxygen. In the later experiments the film of

\* *Trans. Chem. Soc.*, 1865, 18, 44.

† *J. S. C. I.*, 1912, 31, 1103.

‡ Peachey and Leon, *ibid.*, 1918, 37, 55 T.

rubber was under treatment for a period of six months in all, the material being extracted at intervals in order to remove oxidation products and so expose a fresh surface to the action of the oxygen. By fractionally crystallising the oxidised material four compounds were isolated: (a) a viscid resin, neutral in reaction, soluble in most organic solvents, of the composition  $C_{16}H_{26}O_3$ ; (b) an amorphous solid, feebly acidic, soluble in organic solvents, having the formula  $C_6H_9O_2$ ; (c) a brown amorphous substance insoluble in most organic solvents but soluble in alkalis, and having the composition  $C_{11}H_{16}O_4$ ; (d) a reddish-brown amorphous solid insoluble in water, in alkalis, and in all organic solvents with the exception of formic acid, with which, however, it reacted; the composition agreed with the formula  $C_8H_9O_2$ .

As in the case of most other derivatives of caoutchouc, it cannot be said with certainty that of the compounds isolated any one is a pure substance, and consequently deductions as to the constitution of the parent hydrocarbon cannot be drawn from these results.

The effect of allowing resin-free rubber to oxidise under ordinary atmospheric conditions, with full exposure to sunlight, has recently been investigated by Boswell, McLaughlin and Parker;\* after three months approximately 30 per cent. of the rubber had resinified, as evidenced by the formation of acetone soluble material. This was separated into two fractions, one soluble, the other insoluble in carbon disulphide. The soluble portion still possessed properties resembling those of rubber and had the empirical formula  $C_{10}H_{16}O$ ; the insoluble fraction was a hard brittle mass of the composition  $C_{25}H_{40}O_9$ .

The influence of light in conjunction with that of oxygen has already been referred to (p. 61), as has the action of ozone (p. 69).

It has been suggested † that the oxidation of rubber is an example of an autoxidation process in which there is formed an intermediate product, possibly a peroxide, which functions as a catalyst.

As the ozonides of caoutchouc are readily decomposed by water with formation of lævulinic aldehyde, the occurrence of this compound among the products of normal oxidation might, therefore, reasonably be expected. The formation in " tacky " rubber of an aldehydic substance, presumably lævulinic aldehyde, giving the pyrole reaction when heated with ammonium acetate, was indeed observed by Gorter,‡ whose observations have since been confirmed by Bruni and Pelizzola.§ More conclusive evidence has been obtained

\* *I. R. J.*, 1922, 64, 986.

† Ostwald, *J. S. C. I.*, 1913, 32, 179; Kirchhof, *Koll. Zeil.*, 1913, 13, 49.

‡ *Le Caout. et la G. P.*, 1915, 12, 8724.

§ *I. R. J.*, 1922, 63, 415.

by Whitby,\* who prepared and characterised the pyridazine derivative of the aldehyde.

The action of potassium permanganate was studied by Harries † and by Van Rossem, neither of whom was able to isolate oxidation products derived from caoutchouc, although the hydrocarbon itself was transformed into an oily modification. More recently Boswell and Hambleton,‡ by shaking a solution of caoutchouc in carbon tetrachloride with aqueous potassium permanganate for five days, obtained a pasty mass having the composition  $C_{25}H_{40}O$ . This substance was insoluble in alcohol and acetone, soluble in ether, carbon tetrachloride and petroleum ether, and was found to take up an additional atomic proportion of oxygen readily on standing in the air, forming  $C_{25}H_{40}O_2$ .

Hydrogen peroxide was found to yield somewhat similar results,§ the primary product of the reaction having the formula  $C_{30}H_{48}O$ : this on standing in air gave a compound of the formula  $C_{25}H_{40}O_2$ , which is taken as indicating the presence of a nucleus  $C_{30}H_{48}$  in the caoutchouc molecule, the loss of an isoprene residue,  $C_5H_8$ , and addition of oxygen leading to the formation of the more highly oxygenated substance.

### CHROMYL CHLORIDE

When chromyl chloride is added to a solution of caoutchouc in carbon disulphide a definite compound is formed,|| having the empirical formula  $C_{10}H_{16} \cdot 2(CrO_2Cl_2)$ ; the substance, which is a dark solid, insoluble in organic solvents, absorbs moisture on standing in air, undergoing decomposition. On decomposing with water a brown gummy mass separates, which on extraction with ether yields a soluble aldehydic body giving a crystalline derivative with phenylhydrazine melting at about  $92^\circ C$ .

### METALS AND METALLIC SALTS

The influence of copper and its salts in bringing about deterioration of both raw and vulcanised rubber has been recognised for some considerable time. Dewar noted the effect on a rubber washer in contact with a copper pipe, and later Thomson and Lewis ¶ noted the changes occurring when films of vulcanised rubber, sprinkled with metals in the form of filings, were heated at  $60^\circ C$ . for ten days. Copper was found to be most injurious, and in further experiments the deleterious influence of solutions of salts of this metal was

\* *I. R. J.*, 1922, **63**, 742.

† *Ber.*, 1904, **37**, 2708.

‡ *I. R. J.*, 1922, **64**, 984.

§ Boswell, Parker and McLaughlin, *ibid.*, p. 985.

¶ *Chem. News*, 1891, **64**, 169.

|| Spence and Galletly, *J. Amer. Chem. Soc.*, 1911, **33**, 190.

also noted; vanadium chloride, silver nitrate and manganese oxides caused complete deterioration. The harmful effect of copper salts present in cloth used for waterproofing was pointed out by Weber,\* who showed that the presence of as little as 0.01 per cent. of copper was sufficient to cause marked degradation of the rubber coating. Further evidence has been afforded by the experiments of Morgan,† who found that rubber coagulated from latex containing .01 gram copper sulphate per litre quickly developed tackiness and subsequently oxidised. It is evident, therefore, that copper must be rigidly excluded from coming into contact with rubber in the course of preparation on the plantation. The effect of copper salts in hastening deterioration of raw rubber has also been investigated by Eaton,‡ Fox,§ and Whitby.||

The observations of Thomson and Lewis regarding the effect produced by manganese oxides were confirmed by Weber (*loc. cit.*), and latterly by Bruni and Pelizzola,¶ who found that by introducing 1 per cent. of colloidal manganese dioxide into raw rubber tackiness was produced in a few weeks. It is suggested by Bruni and Pelizzola that the presence of manganese may be a contributory factor in causing tackiness sometimes observed in the case of raw rubber, as a number of samples showing this defect were found to contain much more manganese than is normally present.

\* *J. S. C. I.*, 1900, 19, 546.

† *Preparation of Plantation Rubber*, 1913, p. 164.

‡ *Dept. Agric., F. M. S.*, Bulletin No. 17, 1912, p. 27.

§ *Jour. Ind. Eng. Chem.*, 1917, 9, 1092.

|| *Plantation Rubber*, 1920, p. 105.

¶ *I. R. J.*, 1921, 62, 101.

## CHAPTER VIII

### VULCANISATION

INTERESTING as the reactions of caoutchouc described in the foregoing chapter may be from a purely chemical point of view, the changes which occur during the process of vulcanisation are of supreme importance from the industrial standpoint. With very few exceptions rubber goods manufactured at the present time are made up of rubber (associated in most cases with suitable pigments or filling materials) which has been vulcanised by one or other of the available processes. It is perhaps not too much to say that raw rubber is unknown to the average person outside the industry\*; indeed, scientific work is frequently encountered which has been carried out with what is described as "black" or "red" rubber or "rubber tubing," presumably taken as representative samples of rubber.

Of the agents for promoting vulcanisation there are two which are at present of industrial importance—sulphur, and sulphur monochloride ( $S_2Cl_2$ )—both of which were utilised for this purpose more than seventy years ago. Until comparatively recently the vulcanisation by means of sulphur was carried on under much the same conditions as existed in the earliest days of the industry, but during the last decade a good deal of progress has been made in elaborating new or improved methods by which the sulphur is made to function. On the other hand, vulcanisation by means of sulphur chloride is effected in the same manner as was adopted when the process was first introduced.

Of the total output of manufactured rubber goods the proportion made by a process involving the use of sulphur probably exceeds 95 per cent. by weight. The method most commonly employed is that in which the mixture of sulphur and rubber is heated under suitable conditions in order to bring about the change in properties; the same end may be achieved by working at ordinary temperatures according to methods introduced in the last few years, but at present the hot process is the one in use to the greatest extent. Consideration will, therefore, be given in the first place to this type of vulcanisation, and, unless otherwise stated, will be confined to the production of "soft rubber" as distinct from "hard rubber," "vulcanite" or "ebonite," which,

\* Recently, however, raw rubber has been employed for making the soles of footwear and certain other articles, and is therefore becoming familiar to the general public.

as was pointed out in the introductory chapter, results from the prolonged reaction of rubber with high proportions of sulphur.

If a mixture of rubber and sulphur, in the proportion of, say, 90 parts by weight of rubber to 10 parts by weight of sulphur, be heated at  $140^{\circ}\text{C}$ . in a mould between the plates of a press (for details of apparatus see Chapter XIII) for three hours, the sample after removal will be found to have acquired properties differing from those of the original material. The changes which occur are not only physical but chemical in character. Such vulcanised rubber, as we may now call it, if exposed to changes in temperature within a fairly wide range will not be seriously affected. Thus, a moderately low temperature, say  $0^{\circ}\text{C}$ ., will not cause stiffening to take place; moreover, at comparatively high temperatures, say  $100^{\circ}\text{C}$ ., the surface will no longer become tacky.

The material is not "dissolved" by the usual solvents such as benzene, carbon disulphide, etc., and the capacity for swelling in these liquids will be much diminished.

The application of stress produces less deformation than in the case of raw rubber, and after such deformation the material returns almost completely to its original position; in other words, the vulcanised rubber does not exhibit "permanent set" to a marked degree.

In comparison with raw rubber the load necessary to break a piece having unit cross-sectional area is very much greater, as is also the elongation at breaking-point; that is to say, rubber after vulcanisation has a higher tensile strength and may be stretched to a much greater extent before breaking than formerly.

For some considerable time after the discovery of vulcanisation the underlying principles were entirely unrecognised owing to the lack of satisfactory methods of analysis.

It was generally believed that a small proportion of the sulphur was chemically combined and that the rest was unchanged; this assumption was based not on any quantitative data, but merely on the observation that some of the sulphur was removed on boiling vulcanised rubber with alkali. Others regarded the sulphur as being merely absorbed by the rubber, but the character of this "absorption" was not clearly explained, neither was the manner in which the change in properties was effected.

The work of Henriques\* in devising analytical methods, and of Weber† in applying these to a study of the changes taking place during vulcanisation, afforded a further insight into the nature of the process.

\* *Chem. Zeit.*, 1892, 16, 1595, 1623, 1644; 1894, 18, 411, 442, 701.

† *J. S. C. I.*, 1894, 13, 11, 476; 1895, 14, 436.



Weber made up a mixing of 100 parts of Para rubber and 10 parts of sulphur from which he prepared strips 3 mm. thick. A number of these were suspended in a porcelain beaker filled with water, and the whole placed in an autoclave and submitted to temperatures of 120°, 125°, 130°, 135°, 140° C. respectively.

A number of strips were heated at each temperature, and of these one was withdrawn at definite intervals, either half-hourly or hourly. These were extracted for three days with acetone, and the sulphur remaining in the rubber after the extraction determined by the Carius method. The amounts of sulphur in combination with, or at any rate retained by, the rubber were as follows : \*

TABLE VI

Time in mins.	Temperature of Vulcanisation.				
	120° C.	125° C.	130° C.	135° C.	140° C.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
30 . . . . .	0·71	0·71	0·99	1·76	—
60 . . . . .	1·18	1·32	1·44	2·17	—
90 . . . . .	1·31	1·67	2·04	2·36	—
120 . . . . .	1·62	1·91	2·32	3·92	5·07
180 . . . . .	1·78	2·11	2·94	4·18	6·05
240 . . . . .	1·93	2·22	5·00	5·50	—
300 . . . . .	2·25	2·35	5·27	6·74	—
360 . . . . .	2·60	3·80	5·82	6·88	—
420 . . . . .	3·71	4·04	6·04	6·97	—
480 . . . . .	3·94	4·31	6·33	7·13	—

The fixation of sulphur at a given temperature is seen to increase more or less uniformly with increase in time of heating; similarly, for a given time of heating the sulphur fixed increases with the temperature.

The change in physical properties was not examined, but it may be said that the characteristics of vulcanised rubber would be gradually acquired; to take a specific instance, in the case where the temperature was 135° C. the sample heated for 180 minutes would be considered vulcanised from a technical point of view.

Experiments were next carried out in order to determine whether there was a limit to the proportion of sulphur entering into combination with the rubber.

Three mixings were made containing 100 parts of Para rubber and 50, 75,

and 100 parts of sulphur respectively; these were heated in an autoclave for long periods as detailed in Table VI. In each case the product was of the type known as hard rubber or vulcanite; the samples were rasped to give a finely divided powder, and in this condition were extracted with acetone for several days. The sulphur in the extracted sample was determined by the Carius process, the following results being obtained :

TABLE VII

	I.	II.	III.
Rubber . . . . .	100	100	100
Sulphur . . . . .	50	75	100
Time of heating . . . . .	12 hrs.	9 hrs.	8 hrs.
Temperature . . . . .	138° C.	140° C.	140° C.
Sulphur in extracted sample .	33.08 %	33.11 %	32.64 %

Thus it appeared that the proportion of sulphur entering into combination, when calculated on the acetone-extracted sample, was approximately 33 per cent. and that this figure was not exceeded even when sulphur was present in considerable excess.

### COEFFICIENT OF VULCANISATION

Since many technical mixings contain ingredients other than rubber, Weber suggested that the proportion of combined sulphur would be more conveniently expressed as a percentage calculated on the rubber present. Thus, in a mixing containing 90 per cent. rubber and 10 per cent. sulphur, giving on vulcanisation a product containing 4.5 per cent. combined sulphur, the coefficient of vulcanisation would be  $\frac{4.5 \times 100}{90} = 5.0$ . In a case where filling materials were present to the extent of 50 per cent., the rubber content being 45 per cent. and the combined sulphur after vulcanisation 2.25 per cent., the coefficient would be  $\frac{2.25 \times 100}{45} = 5.0$ ; the similarity in the degree of combination of the rubber with sulphur in the two mixings is more apparent when the proportion of combined sulphur is expressed in this way.

### THEORY OF VULCANISATION

From the results of his investigation Weber was able to formulate a theory of vulcanisation, the first to be substantiated by adequate experimental data.

In the first place, the fact that a proportion of sulphur was taken up by the rubber in such a way that it was no longer extractable on prolonged treatment with solvents for sulphur was regarded as evidence that a chemical combination had taken place. Further, since the reaction was not accompanied by evolution of hydrogen sulphide, the process must be one of addition and not of substitution, as had been suggested.\* The limit of combination with sulphur was shown to be reached in the formation of a compound having the empirical formula  $C_{10}H_{16}S_2$ , polyprene disulphide, the proportion of sulphur in which should be 32.00 per cent., a figure corresponding closely with the average of that found in the samples made by heating rubber with excess of sulphur, namely, 32.94 per cent.

This was regarded as the highest member of a series of polyprene sulphides of which the lowest member was a compound represented by the formula  $(C_{10}H_{16})_{10}S$ , containing 2.29 per cent. sulphur. Such a view received support from the observation that the characteristics of vulcanisation first became apparent when the combined sulphur was present to the extent of 2 to 2.5 per cent.† It was recognised that no other evidence could be obtained of the formation of separate members of this series, as the alteration in properties from unvulcanised rubber to soft vulcanised rubber and then to hard rubber (vulcanite) was a gradual one, unmarked by sudden changes in the character of the product at any stage in the process. It is true that, when Weber's figures for the combination of sulphur with increase in time of heating were plotted in the form of a graph, there were breaks noticeable at various points, but these breaks did not occur at the same points with different temperatures of vulcanisation. Subsequent work has shown that the irregularities must have been due to errors in timing, owing to the difficulty of opening and closing the autoclave in which the samples were heated, and the necessity to add fresh water from time to time.

While these experiments indicated that the progress of vulcanisation was accompanied by a chemical reaction, the formation of a definite chemical compound did not appear to afford an entirely adequate explanation of the marked change in properties brought about by the action of such a small proportion of sulphur as enters into combination. Weber himself appeared to regard the reaction as bringing about peptisation of the rubber colloid in a manner somewhat resembling that in which egg albumen is coagulated with certain reagents.

It is interesting to note that what was probably the first theory of vulcanisation was of a purely physical character. Brande in 1852, lecturing before the

\* E. g. Payen, *Compt. rend.*, 1852, 34, 2.

† Weber, *loc. cit.*, p. 91.

members of the Royal Institution,\* remarked, " May we not therefore conclude that under the influence of sulphur and heat, the rubber acquires its new and distinct properties, not by actual chemical combination with a minute portion of sulphur, but by the assumption of a new molecular condition; that, like phosphorus it has assumed an allotropic state? "

Later, Höhn † adopted a somewhat similar attitude, holding that the vulcanisation of rubber was not due to any direct chemical action, but that the sulphur in the molten state was merely absorbed by the cells of the rubber, forming a kind of alloy with it.

The ideas formulated by Brande and Höhn among others may be regarded as the precursors of the adsorption theory which was propounded by Wolfgang Ostwald in 1910.‡ After a comprehensive survey of the results of previous workers, Ostwald sought to show that the available data were more in accord with a process of adsorption of sulphur by rubber than with one in which sulphur entered into chemical combination with the rubber. The chief facts on which he based this hypothesis were as follows: (1) In all vulcanised rubber there is present free sulphur which would not be expected if a chemical reaction were involved. (2) According to Höhn, vulcanised rubber on sufficiently prolonged extraction could be freed entirely from sulphur. (3) The rubber always takes up sulphur in a purely additive manner; no substitution takes place. (4) A continuous series of addition products is formed, the first and last members of which have no definite stoichiometrical composition. (5) The amount of sulphur absorbed by the rubber increases with the previous mechanical treatment; § this could be explained by assuming rubber to consist of a two-phase system, the degree of dispersion of the disperse phase, and hence the adsorptive capacity, being thus increased. (6) The capacity for taking up sulphur increases with rise of temperature, and the temperature coefficient is more nearly in accord with an adsorption process. (7) The fixation of sulphur at a given temperature does not take place uniformly, as the breaks in Weber's curves show; this phenomenon is frequently met with in the adsorption of water by certain gels, for example, silicic acid. (8) Adsorption proceeds in accordance with the exponential equation  $\frac{x}{a} = kc^m$ , where  $x$  is the weight of adsorbed substance,  $a$  is the weight of adsorbent,  $c$  is the initial concentration of the substance which is adsorbed, and  $k$  and  $m$  are constants.

The views put forward by Ostwald led to a more intensive study of the vulcanisation process than had hitherto been given, and a number of important

\* Cf. Hancock, p. 60.

† *Koll. Zeit.*, 1910, 6, 136.

‡ *Gummi Zeit.*, 1899, 14, 17, 33.

§ Cf. Axelrod, *Gummi Zeit.*, 1909, 24, 352.

results were quickly forthcoming, the points raised by Ostwald being dealt with in detail.

(1) With regard to the assumption that free sulphur was always present in vulcanised rubber, this was quite true with regard to rubber heated with sulphur for a sufficient time to allow of the characteristics of vulcanisation being acquired. It was shown, however, by Spence and Young \* that on heating a mixture of 100 parts rubber, first extracted with acetone to remove resins, with 10 parts sulphur for thirty hours at 135° C. and ten hours at 155° C. respectively, no sulphur could be extracted on treatment with acetone.†

(2) The statement of Höhn that all the sulphur could be extracted from vulcanised rubber is one that at the time was entirely unsupported by the results of other workers. Harries and Fonrobert ‡ have since recorded the results of experiments in which Para rubber with 10 per cent. of sulphur was vulcanised for thirty minutes at 145° C., and a 500 gram lot of the product extracted for sixty days with acetone. At the end of this period the residue contained only 0.29 per cent. of sulphur, which the authors regarded as negligible; the material after treatment did not possess the same degree of elasticity as before, and on further vulcanisation did not give a satisfactory product. In attempts to obtain confirmation of this behaviour, Stevens § was unable to reproduce the results. Samples of Para rubber and sulphur in proportions similar to those employed by Harries were vulcanised for nineteen minutes and thirty minutes respectively at 145° C. The vulcanised samples were then extracted with acetone and portions removed at the end of one week, two weeks, four weeks, and nine weeks. The combined sulphur was determined in each sample, with the following result :

TABLE VIII

After extracting for	Combined sulphur in sample vulcanised for	
	30 mins.	19 mins.
1 week	1.54	0.94
2 weeks	1.54	0.96
4 „	1.47	0.95
9 „	1.55	0.96

\* *Koll. Zeit.*, 1912, 11, 28.

† *Ber.*, 1916, 49, 1196, 1390.

‡ Cf. also Spence, *ibid.*, 1912, 10, 299.

§ *J. S. C. I.*, 1919, 38, 192 T.

Other samples were treated in a similar manner, but in all cases sulphur remained in the extracted sample even after nine weeks' extraction.

Attempts have also been made to remove the sulphur by chemical means, as in the experiments of Hinrichsen and Kindscher,\* who heated vulcanised rubber swollen in benzene in an autoclave with alcoholic alkali in the presence of finely divided metals, such as zinc and copper. In this way the combined sulphur was reduced from 4.35 per cent. to 1.47 per cent. in the case of the sample heated at ten atmospheres pressure.

Alexander † has pointed out, however, that their results were obtained with mixings of which they did not know the composition, and has repeated their experiments with mixings made up by himself. Samples with various coefficients of vulcanisation were employed, and these were heated in an iron autoclave with copper, zinc, calcium and magnesium respectively. In no case was a reduction in the coefficient of vulcanisation observed, although Alexander points out that at the comparatively high temperatures at which the experiments were carried out there is a danger of a degradation of the rubber occurring with formation of acetone-soluble matter. Alexander concludes that removal of combined sulphur by metals or alkalis cannot be effected, a similar conclusion having been arrived at subsequently by Porritt.‡

(3), (4) The purely additive nature of the process was never really questioned after Weber's experiments showed the absence of hydrogen sulphide from the products of reaction. A chemical explanation is not difficult of acceptance, since sulphur may reasonably be supposed to form an addition compound by combination at one of the double bonds of the caoutchouc molecule. The statement that none of the compounds formed by the combination contained sulphur in stoichiometrical proportion was not in conformity with Weber's experiments, which certainly showed that the highest limit of combination corresponded closely with the compound  $C_{10}H_{16}S_2$ . Weber, however, did not conclusively prove that combination would not take place on further heating, as only one sample vulcanised for a definite period was examined. The finality of the reaction was, however, clearly demonstrated by Spence and Young,§ who vulcanised mixtures of acetone-extracted Para rubber (63 parts) and sulphur (37 parts) at 135° C. for periods varying from one to thirty hours. At the end of 18½, 20, 25, and 30 hours, the proportion of sulphur in the residue remaining after extraction of free sulphur was 31.75, 31.97, 31.91, 31.97 respectively; the sample after twenty hours' vulcanisation still contained

\* *Koll. Zeit.*, 1912, 10, 146; 1912, 11, 38.

† *Chem. Zeit.*, 1912, 36, 1289, 1340, 1358.

‡ *The Chemistry of Rubber*, 1914, Gurney and Jackson, p. 63.

§ *Koll. Zeit.*, 1912, 11, 28.

3.80 per cent. of free sulphur, so that the cessation of the reaction was not due to lack of sulphur.

The formation of a definite compound was further emphasised by Hinrichsen and Kindscher,\* who heated rubber in cumene at 170° C. with proportions of sulphur increasing to 400 per cent. calculated on the rubber present. In all cases a dark brown pulverent substance was obtained containing not more than 32 per cent. of combined sulphur.

(5) With regard to the statement of Axelrod, that mechanical working affected the rate of combination with sulphur, Weber had previously enunciated as a general principle that rubber containing a certain proportion of sulphur gave the same chemical result on vulcanisation for a given time whether it had previously been subjected to mastication for a prolonged or normal period,† although the physical results might be widely different.

That this was actually the case was shown by Spence and Ward,‡ who found that by employing a mixing containing 100 parts of Hard Fine Para rubber, and 10 parts of sulphur, the rate of combination with sulphur was the same whatever the mechanical treatment, that is to say, whether the rubber was over-milled or normally milled. In order to obtain products of equal tensile properties, however, it was necessary to vulcanise for a longer period in the case of the over-milled sample than in the case of the normally milled sample, and thus a higher coefficient of vulcanisation was obtained.

(6), (7), and (8). The rate of the fixation of sulphur at a given temperature, judging by the results of Weber, was not uniform, and the breaks in the curve were held to support the adsorption theory. Spence and Young§ repeated some of Weber's experiments and sought to eliminate all sources of error. In the first place the lack of uniformity might be due to reaction of sulphur with the non-caoutchouc substances proceeding at a different rate from that of the caoutchouc portion; Spence and Young, therefore, worked with acetone-extracted rubber. Again, the difficulty attending the opening and closing of the autoclave, with a consequent loss in accuracy of controlling the time of heating, was overcome by employing as source of heat a bath of glycerine heated by the vapour of boiling xylene.|| The rubber in thin strips was clamped in a mould consisting of two concentric metal rings, and the mould after warming inserted in the glycerin bath; a number of moulds could be employed and taken out as required after the requisite heating period. In this way the time and temperature of heating could be regulated with precision.

\* *Koll. Zeit.*, 1912, 11, 191.

† *The Chemistry of India Rubber*, p. 94.

‡ *Koll. Zeit.*, 1912, 11, 274.

§ *Ibid.*, 1912, 11, 28.

|| Spence and Young, *Chem. Zeit.*, 1912, 36, 1162.

## VULCANISATION

Samples of a mixing of 90 parts Pale Ceylon rubber with 10 parts sulphur were heated at 135° C. and samples taken at intervals; combined sulphur was determined, and the results obtained plotted against time of heating gave a smooth curve.

A further experiment was carried out in which a similar mixing was heated at 155° C., a smooth curve being obtained as in the former case.

The percentage of combined sulphur at various times of heating are given in the following table :

TABLE IX

Temperature = 135° C.			Temperature = 155° C.		
Time of heating.	Combined sulphur.	$K = \frac{x}{t}$	Time of heating.	Combined sulphur.	$K = \frac{x}{t}$
Hrs.			Hrs.		
0.5	0.22	0.440	0.5	1.62	3.24
1.0	0.44	0.450	1.0	3.35	3.35
2.0	0.91	0.455	1.5	5.46	3.64
3.0	1.40	0.466	2.0	6.97	3.48
4.0	1.90	0.475	2.5	7.62	3.05
5.0	2.38	0.476	3.0	7.97	—
6.0	2.89	0.481	3.5	8.16	—
7.0	3.19	0.478	5.0	8.27	—
8.0	3.82	0.477	9.0	8.29	—
9.0	4.48	0.477	10.0	8.29	—
10.0	4.86	0.480			
15.0	7.20	0.480			
20.0	8.46	—			
30.0	8.46	—			

The velocity coefficient  $K$  of the reaction was calculated from the equation  $K = \frac{x}{t}$ , where  $x$  is the percentage of sulphur entering into combination in a given time  $t$ , in this case thirty minutes.

The average value for  $K$  at 135° C. was thus found to be 0.477, and at 155° C. was 3.352. The temperature coefficient of the reaction velocity calculated from Van't Hoff's equation was found to be 2.65 for ten degrees increase in temperature, a value in conformity with that obtaining in the case of a chemical reaction.

In an extension of these experiments to the study of vulcanisation at lower temperatures the same authors \* obtained the following results :

\* Spence and Young, *Koll. Zeit.*, 1913, 13, 265.



TABLE X  
COMBINED SULPHUR (%).

Time in days.	50 deg.	55 deg.	60 deg.	65 deg.	70 deg.	75 deg.
5 . . .	0.04	0.08	0.098	0.197	0.384	0.495
15 . . .	—	—	—	0.564	1.13	1.71
25 . . .	0.15	0.36	0.57	—	—	—
35 . . .	—	—	—	1.46	2.60	3.80
50 . . .	0.25	0.65	1.03	—	—	—
65 . . .	—	—	—	2.55	4.91	7.42
80 . . .	0.45	1.10	1.86	3.37	6.05	8.81
90 . . .	—	—	—	—	—	9.36

The rubber used in these experiments consisted of acetone-extracted rubber to which 1 per cent. of acetone soluble material was added.

It will thus be seen that at temperatures of 50° C. and over vulcanisation as evidenced by combination with sulphur takes place, the rate increasing with rise in temperature.\*

The temperature coefficient of the whole series gave an average value of 2.84, which, like the previous one, lies within the limits for that associated with a chemical reaction.

Experiments by Skellon † also indicate the chemical nature of the reaction. Skellon vulcanised mixings containing increasing proportions of sulphur, and plotted the combined sulphur contents per 100 parts of rubber against the initial sulphur content; curves were thus obtained for different times of heating. The curves took an upward tendency until a certain point was reached, when flattening occurred, and this position was taken to indicate the point at which the rubber was saturated with respect to sulphur.

Up to this maximum point the curves were shown to be of the type  $\frac{y}{m} = ac$ , where  $y$  = amount of sulphur combined,  $m$  = reacting masses,  $a$  = constant,  $c$  = concentration of sulphur in rubber, and were thus of the type characteristic of a chemical reaction and not of an adsorption phenomenon.

Further evidence in favour of the chemical combination of sulphur during vulcanisation is afforded by the experiments of Spence and Scott,‡ who found that when bromine reacts with vulcanised rubber instead of combining in the proportion of four atoms of bromine for every  $C_{10}H_{16}$ , the resulting compound

\* Spence had previously shown that vulcanisation did not occur at temperatures up to 40° C. —*Koll. Zeit.*, 1912, 10, 299.

† *The Rubber Industry*, 1914, p. 172.

‡ *Koll. Zeit.*, 1911, 8, 304.

contains bromine in less proportion than is required to form the tetrabromide, the balance being made up of the equivalent of sulphur. Similarly in the formation of the nitrosite coefficients with increasing vulcanisation, decreasing proportions of nitrous gases are taken up. Harries \* has stated that sulphur does not pass into the hydrochloride prepared from vulcanised rubber, but this is in reference to a sample which was said to yield all its sulphur to acetone on extraction. On keeping in a warm place for a long time the sulphur becomes unextractable and is found in the hydrochloride prepared in the usual way. From this we may conclude that vulcanised rubber, in the ordinarily accepted sense of the term, yields a hydrochloride in which sulphur is present in combination.

It is also interesting to note that the hydrocaoutchouc prepared by Staudinger and Fritsch (see p. 85) by hydrogenating caoutchouc in presence of a platinum catalyst is not capable of vulcanisation, and it appears logical to conclude that this is due to the elimination of the double bonds, as a result of which a sulphur addition product cannot be formed. The hydrogenation was, however, carried out at a temperature of 270° C., under which conditions it is unlikely that the caoutchouc molecule would remain unaffected. It would be of greater interest to know whether the hydrocaoutchouc prepared by hydrogenation at the lower temperature employed by Pummerer and Burkard (*loc. cit.*) is capable of vulcanisation, but this has not yet been investigated.

While the available evidence is overwhelmingly in favour of the occurrence of a chemical reaction during vulcanisation, it can hardly be said that the possibility of a physico-chemical theory of vulcanisation is entirely excluded. What does appear to be proved is that the process is not one consisting merely of an adsorption of sulphur by rubber. It may be noted that a study of the velocity of extraction of sulphur from vulcanised rubber by means of acetone led Spence † to conclude that part of the "free" sulphur was adsorbed and that possibly adsorption preceded the chemical reaction. The difficulty of removing the last portions of sulphur may, however, conceivably be due to the slowness of penetration of the interior portions of the rubber particles by the acetone, which would lead to a decrease in velocity of extraction from the surface inwards. If it is accepted that heating with a sufficiently high proportion of sulphur leads to the formation of a definite compound, there is no reason to suppose that this reaction does not take place when proportions of sulphur such as are used in producing soft rubber goods, *i.e.* less than 10 per cent., are employed. The fixation of sulphur up to 32 per cent. takes place uniformly, and there is no indication that at any particular stage the reaction changes in character.

\* *Ber.*, 1916, 49, 1196.

† *Koll. Zeit.*, 1911, 9, 300.

The manner in which the effect of vulcanisation is produced by the combination of the rubber with small proportions of sulphur remains to be elucidated, and it cannot be said that the question is at present capable of explanation. The assumption that a series of sulphur addition products is formed does not explain why the properties of the rubber as a whole are affected by even lower proportions of sulphur than are normally employed in manufacturing operations.

It is known that vulcanised rubber does not "dissolve" as does the raw material. That quite small proportions of sulphur are sufficient to cause insolubility has been shown by Stevens,\* who heated samples containing 90 parts rubber and 10 parts sulphur for 30, 40, 50, and 60 minutes at 125° C. After exhaustive extraction with acetone the residual sulphur was determined and found to be 0.27, 0.39, 0.45, and 0.54 per cent. respectively. The resistance to solvents increased with time of heating, the thirty-minute sample dissolving readily, while the sample heated for sixty minutes swelled, but was not disintegrated on shaking; on standing for a considerable time, however, solution was effected. These samples had not been brought to the physical condition characteristic of technically vulcanised rubber, and a further series of experiments was carried out, employing rubber-sulphur mixings heated to give "combined" sulphur contents of 3.80 per cent. and 8.64 per cent. respectively. These were exhaustively extracted with benzene for one week and the proportion dissolved by benzene determined; sulphur was estimated in the benzene-extracted sample. The following results were obtained:

Proportion dissolved by benzene.	Sulphur before extraction.	Sulphur after extraction.
30.8% 13.7	3.80% 8.64	3.85% 8.35

Thus the higher the proportion of combined sulphur the more resistant is the sample to the action of solvents; further, the portions which dissolve out are approximately of the same sulphur content as those which remain undissolved.

The effect of progressive vulcanisation is, therefore, to render the product increasingly resistant to the action of solvents, but a sharp line of demarcation between solubility and insolubility cannot be drawn. Nevertheless, it is not possible with the aid of solvents to separate vulcanised rubber into fractions containing sulphur in different proportions. Solubility experiments, therefore, do not furnish evidence that in vulcanised rubber in which sulphur is

\* *J. S. C. I.*, 1919, 33, 195 T.

combined in proportions which are not stoichiometric there is present a definite chemical compound associated either with unchanged rubber or with a compound of a lesser degree of vulcanisation. At the same time the possibility is not excluded that such a system is actually present; indeed Ostromisslenski \* considers vulcanisation as a process in which only a small proportion of the rubber enters into combination with sulphur to form a compound in which the unchanged rubber is swollen or adsorbed.

The reverse condition may equally well obtain, in which the compound formed is adsorbed by the unchanged rubber. Opposed to a theory such as this is the fact that fully vulcanised rubber dispersed throughout unvulcanised rubber does not confer upon the mixture the property of vulcanised rubber, even after heating.

A process of polymerisation has been suggested by Axelrod † to account for the change in properties. Vulcanisation is regarded as a process in which there occurs a simultaneous "depolymerisation" by means of heat and a "polymerisation" due to the sulphur with simultaneous formation of a sulphur addition product. It is not clear whether a purely chemical polymerisation is to be understood, or whether the change is to be regarded as the reverse of the effect noted when the rubber is submitted to mechanical working, a change which may be followed by examining the viscosity of the rubber in solution.

An explanation based on a process of chemical polymerisation or physical aggregation, or a combination of the two, is not altogether unreasonable, since caoutchouc itself may be regarded as the product of the polymerisation of isoprene. Thus a mobile liquid soluble in all organic solvents may pass spontaneously into an elastic mass, insoluble in many liquids capable of dissolving the parent hydrocarbon. It is conceivable that caoutchouc itself may be further polymerised to form a hydrocarbon still more resistant to solvents, and with more marked elastic properties. So far it is doubtful whether such polymerisation has been induced by agents of which it can be said with certainty that they do not enter into chemical combination; some of the synthetic caoutchoucs, it is true, do not swell or dissolve as readily as does natural rubber, and it may be that in this case polymerisation has proceeded farther than is necessary merely to produce normal caoutchouc. Sulphur itself does not appear to be suitable as a polymerising agent for converting isoprene into caoutchouc, although this cannot be taken as proving conclusively that it does not effect a similar change in the case of caoutchouc already formed.

There is abundant evidence that in hot vulcanisation there are being exerted, as postulated by Axelrod, two opposing influences, of which the heat

\* *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1453.

† *Gummi Zeit.*, 1909, **24**, 352.

tends to produce a degradation of the rubber, whilst the sulphur tends to impart improved properties. This is, however, in no sense an explanation of the nature of the change induced by the sulphur.

Kirchhof \* puts forward the theory that vulcanisation consists essentially in the transformation of rubber from a relatively unstable to a stable form, the chemical combination of sulphur being regarded as a subsidiary process.

Harries † has propounded a somewhat similar hypothesis, the caoutchouc in raw rubber being regarded as a "metastable" modification which passes into a stable modification in presence of sulphur. Vulcanisation is assumed to take place in two stages, the first or primary vulcanisation consisting in the passage into the stable form accompanied by adsorption of sulphur. This sulphur can be extracted quantitatively, but if, before extraction, the sample is kept in a warm place for some time, a proportion of the sulphur is then fixed in such a way that subsequent treatment with acetone does not effect its removal; the second stage of the process is termed post-vulcanisation. The primary vulcanisation is said to give a product which after removal of sulphur differs from raw rubber in that it is less readily attacked by ozone and cannot again be vulcanised satisfactorily. Whether the product obtained by this primary vulcanisation can be said to be vulcanised in the usually accepted sense of the term is not clear, since no mechanical tests were applied. The position still appears to be that rubber, properly vulcanised with the aid of sulphur, has not yet been obtained by a process which does not involve the fixation of sulphur in a manner which can hardly be other than a chemical combination.

#### RELATIVE ACTIVITY OF VARIOUS FORMS OF SULPHUR

The existence of sulphur in many modifications has led to the suggestion that one of these may be more active, and that in order to ensure vulcanisation it is necessary for conditions to be such as to favour the formation of this active modification. Thus, Erdmann ‡ states that melted sulphur on cooling to 160° C. contains a highly reactive, unstable analogue of ozone, thio-iozone  $S:S:S$ . Vulcanisation would in this case involve the formation of the thio-ozonide of caoutchouc. As this thio-ozone is stable only at high temperatures, this does not afford an explanation of the action of sulphur at temperatures

\* *Koll. Zeit.*, 1913, 13, 49; 1914, 14, 35; 1920, 26, 168.

† *Ber.*, 1916, 49, 1196; Harries and Fonrobert, *ibid.*, 1916, 49, 1196, 1390.

‡ *Annalen*, 1908, 362, 133.

lower than those at which it is stable; in anycase this hypothetical thio-ozone has not been isolated.

A form of sulphur believed to be trithio-ozone has recently been prepared by Bedford and Sebrell \* by passing sulphur dioxide and hydrogen sulphide into benzene cooled to 10° C. or lower. In this way a bright yellow deposit is obtained which gradually changes to plastic sulphur similar to that obtained on pouring molten sulphur into water; on allowing to stand the product crystallises. If the freshly precipitated sulphur is washed with cold solvent and then introduced into a rubber cement, vulcanisation takes place at ordinary temperatures. Since this modification is stable only at low temperatures, the possibility of its formation during hot vulcanisation is excluded.

The relative activity of certain of the readily obtainable modifications of sulphur has been investigated by Twiss,† who has shown that although differences are noticeable in the case of  $S\lambda$ ,  $S\mu$ , and  $S\pi$ , these are of very small magnitude.

That vulcanisation with the aid of sulphur may be accomplished at ordinary temperatures has been shown by Peachey,‡ who adopted the principle of forming the sulphur *in situ* by exposing rubber alternately to hydrogen sulphide and sulphur dioxide. The sulphur formed by the interaction of these two gases effects vulcanisation instantaneously, the product being characterised by the ordinary features of hot vulcanised rubber, the tensile properties being improved and part of the sulphur entering into combination with the rubber. The enhanced activity of the sulphur liberated is generally explained on the grounds that it is in the "nascent" state, although this has been contested by Bedford and Sebrell,§ who attribute it to the formation of thio-ozone.

It has been suggested that in ordinary hot vulcanisation the heating of the rubber with sulphur is necessary in order to bring about secondary reactions with the accessory substances present in the rubber in such a way that ultimately the sulphur is reproduced in an active state.

For example, Dubosc || has suggested that during vulcanisation the rubber resins react with sulphur to form hydrogen sulphide; other accessory substances containing oxygen also react to form sulphur dioxide, which with

\* *J. I. E. C.*, 1922, **14**, 29.

† *Ann. Rep. Applied Chem.*, 1919, **4**, 327. Cf. also Twiss and Thomas, *J. S. C. I.*, 1921, **40**, 48 T.

‡ E.P. 129826; Peachey and Skipsey, *J. S. C. I.*, 1921, **40**, 5 T.

§ *J. I. E. C.*, 1922, **14**, 29.

|| *I. R. J.*, 1915, **49**, 667.

the hydrogen sulphide yields "colloidal" sulphur. While the formation of hydrogen sulphide from rubber resins and sulphur at vulcanising temperatures is known to occur, the reaction involving the formation of sulphur dioxide is not capable of demonstration. With regard to the suggestion that sulphur in colloidal form would cause vulcanisation, it may be remarked that sulphur, even in colloidal form, will not vulcanise rubber latex under ordinary conditions, but the same procedure must be adopted as when dealing with ordinary rubber, *i. e.* the mixture must be heated under suitable conditions.\*

### VULCANISATION IN SOLUTION

Not only is rubber in the plastic state capable of being vulcanised, but the reaction may be brought about in solution. Hinrichsen and Kindscher (see p. 28), by heating rubber and sulphur at 170° C. in cumene solution, succeeded in producing compounds of rubber and sulphur. These were not of interest from a technical point of view, since no attempt was made to produce a solution which would yield on evaporation a film of rubber possessing satisfactory mechanical strength. It was found by Helbronner and Bernstein † that on exposing a solution of rubber and sulphur to ultra-violet light vulcanisation proceeded at ordinary temperatures. In this way a viscous liquid was obtained which on evaporation yielded a film which possessed all the characteristics of vulcanised rubber. It was suggested that such "solutions" of vulcanised rubber could be employed as cements, in which case the surfaces treated would be united by a vulcanised film instead of by a film of raw rubber, such as would result from the application of ordinary rubber cement.

By immersing vulcanised rubber in a suitable solvent gels may be obtained, but such gels possess great rigidity and cannot be applied as cements. By heating for a long time with excess of solvent gels of vulcanised rubber are dispersed, but the rubber undergoes a process of degradation, and the film left on evaporating the solvent does not possess satisfactory mechanical strength.

By heating solutions of rubber with sulphur at temperatures similar to those employed for hot vulcanisation, Stevens ‡ has succeeded in obtaining mobile sols which will yield on evaporation films of vulcanised rubber. These films possess satisfactory tensile properties and, like normally vulcanised rubber, cannot be re-dissolved in the usual solvents if the coefficient of vulcanisation is sufficiently high. The rate of combination of sulphur with rubber in solution is lower than is the case when the rubber is plasticised without addition of solvent. With a particular proportion of rubber and sulphur

\* Schidrowitz, E.P. 193451.

† *Rubber Industry*, 1914, p. 156.

‡ *J. S. C. I.*, 1921, 40, 186.

the rate of vulcanisation decreases uniformly with increasing proportions of solvent; the progress of vulcanisation may be hastened by addition of organic accelerators.\*

The chief difficulty attending the preparation of sols of vulcanised rubber is to regulate the conditions so as to avoid the formation of a gel, which may happen if the concentration of the rubber in the original sol is too high; such gels would not be capable of application as cements or as a means of proofing fabric. On the other hand, a too low concentration will inhibit vulcanisation to such an extent that a mechanically weak film results on evaporation; apart from this a dilute sol of vulcanised rubber would not possess any commercial interest.

Sols of vulcanised rubber may also be prepared by the aid of the Peachey process, a solution of sulphur dioxide in benzene or other solvent being added to a solution of rubber in benzene saturated with hydrogen sulphide. In employing this method gel formation may take place rapidly if the concentration of rubber is comparatively high; the formation of a gel is retarded by adding pyridine,† and hastened by the addition of quinone.‡

### VULCANISATION OF RUBBER IN LATEX

The process of vulcanisation in solution results, under favourable conditions, in the formation of a mobile sol which will, on evaporation, deposit a film of already vulcanised rubber. Under these circumstances cloth proofed with such a sol would not have to be treated further after the application of the film. In this way delicate fabrics, or fabrics coloured with dyes which would be injured by hot vulcanisation, could be proofed satisfactorily. A process which avoids the employment of organic solvents, and which has been named the "Vultex," process, has recently been devised by Schidrowitz.§ This consists in vulcanising the rubber while still in the form of latex, under such conditions that coagulation does not take place. The latex, containing a suitable anti-coagulant such as sodium sulphite, is mixed with either precipitated or colloidal sulphur or with a polysulphide. Substances such as casein may be added to act as protective colloids, and vulcanisation may be expedited by the addition of organic accelerators. Filling agents and colouring matters may be added and the whole then heated in an autoclave, when vulcanisation proceeds, although the latex does not alter in respect to its appearance. An aqueous suspension of vulcanised rubber is thus obtained which may be employed for the purpose of impregnating fabric, or the vulcanised rubber may be coagulated by addition of acetic or other acid.

\* E.P. 164770.

† E.P. 129826.

‡ E.P. 190051.

§ E.P. 193451.



Aqueous suspensions have also been prepared by Alexander \* from rubber, previously vulcanised, which was first swollen in a suitable solvent and then heated under pressure with an aqueous alkaline solution.

#### VULCANISATION BY MEANS OF SULPHUR CHLORIDE

Sulphur monochloride,  $S_2Cl_2$ , comes next in importance to sulphur as an agent for promoting the change in properties characteristic of vulcanisation.

In this case the action takes place at ordinary temperatures, and the method of application therefore differs from that generally adopted when sulphur is employed.

The rubber in the form of thin films is either exposed to an atmosphere charged with the vapour of the liquid or is immersed in a dilute solution of the sulphur chloride in a suitable solvent, *e. g.* naphtha or carbon tetrachloride.

The effect of the treatment is most apparent at the surface of the rubber, and the process is therefore suitable only for dealing with comparatively thin sheets.

The action of sulphur chloride on rubber is comparable in most respects with that of sulphur, in that a small proportion of the reagent will cause a marked change in properties.

At one time the action of sulphur chloride was thought to be due to the sulphur present, the chlorine taking no part in the reaction; others held that the chlorine was the active constituent. Weber,† however, showed that when rubber was immersed in a solution of sulphur chloride in carbon disulphide a product was obtained in which the sulphur and chlorine were present in the proportions corresponding to the formula  $S_2Cl_2$ . Weber also showed that, as is the case with sulphur, the maximum amount of sulphur chloride taken up by the rubber bears a stoichiometric relationship to the amount of rubber present. In carrying out his experiments Weber dissolved purified rubber in carefully dried benzene, and excess of a solution of sulphur chloride in benzene was added. The liquid gradually thickened and then set to a jelly, which was broken up and washed with benzene until free from excess sulphur chloride. The residue was extracted in a Soxhlet apparatus with carbon disulphide, and after drying was analysed and found to correspond to a compound of the composition  $C_{10}H_{16}S_2Cl_2$ . Subsequent workers, however, have failed to confirm this statement, as in no case has a product been obtained containing more than one-half molecular proportion of sulphur chloride for each  $C_{10}H_{16}$ . Hinrichsen and Kindscher,‡ for example, took weighed amounts of rubber in benzene and added measured volumes of sulphur chloride solutions of known

\* E.P. 14681, 1905.

† J. S. C. I., 1894, 13, 14.

‡ Koll. Zeit., 1910, 6, 202.

concentration. After remaining in contact for three weeks the proportion of sulphur chloride left in the solution was determined, and from this the amount taken up by the rubber was deduced; the results indicated that a compound of the composition  $(C_{10}H_{16})_2S_2Cl_2$  was formed. Bernstein,\* by following Weber's procedure of isolating the vulcanisation product and purifying by extraction with carbon disulphide, obtained a fine powder having a composition similar to that of Hinrichsen and Kindscher. Working in dilute solutions with considerable excess of sulphur chloride the proportion fixed did not on any occasion exceed that corresponding to the formula  $(C_{10}H_{16})_2S_2Cl_2$ .

It is probable that the high proportion observed by Weber was due to decomposition of sulphur chloride by moisture present with formation of sulphur insoluble in carbon disulphide. The hydrogen chloride liberated simultaneously would form an additive compound with the rubber, and thus both sulphur and chlorine would be found in approximately the proportions in which they exist in the sulphur chloride; this would account for the chlorine content being high as well as the sulphur.

The question of the state of the sulphur chloride in the rubber has been the subject of some controversy, and, as in the case of hot vulcanisation with sulphur, both the chemical and adsorption theories have been advocated.

Weber regarded the action of sulphur chloride on rubber as analogous to that with other unsaturated hydrocarbons as described by Guthrie.†

It certainly does appear difficult to believe that rubber vulcanised by means of sulphur chloride contains this substance in any other state than that of chemical combination; there is no indication of the presence of a pungent liquid which fumes in air, and, moreover, decomposition does not occur on immersing the rubber in water.

An experiment carried out by Weber ‡ goes to show that chemical combination actually does occur. A dilute rubber solution was treated with sulphur chloride in a proportion considerably in excess of that necessary to effect vulcanisation. The concentration was such that gelling did not take place after standing for some time. A solution of rubber was then added and the whole mixed; the rubber obtained on precipitation was treated with a solvent and a proportion was found to dissolve. Another rubber solution was taken and sulphur chloride added to give a proportion on the rubber equal to that which was present when the two previous solutions were mixed. In this case the rubber obtained on precipitation did not dissolve on treatment with benzene. If the process were one of adsorption one would expect that

\* *Koll. Zeit.*, 1912, **11**, 185.

† *Annalen*, 1860, **113**, 270.

‡ *J. S. C. I.*, 1894, **13**, 14.

on adding a solution of rubber to another containing rubber and sulphur chloride the sulphur chloride would be adsorbed on the added rubber and the effect of vulcanisation be produced on the whole of the rubber.

Bysow \* carried out experiments in order to find whether sulphur chloride was removed completely from a petroleum ether solution by rubber. The concentration of sulphur chloride employed was 1.8 gr. in 100 c.c. of petroleum ether, and in each 100 c.c. there was immersed a strip of purified rubber 0.5 mm. thick and weighing 0.5 gr. Samples were withdrawn at intervals and sulphur determined in the washed and extracted sample; the results indicated that sulphur chloride was gradually taken up by the rubber until after ninety minutes an equilibrium was established, sulphur chloride still being present in the solution. The sample then contained only 0.45 per cent. of sulphur, and therefore the cessation of the fixation could not be due to the complete conversion of the rubber into the additive compound, which would contain 15.7 per cent. of sulphur. There was thus an indication that the phenomenon might be one of adsorption, but it might equally be due to formation of a vulcanised layer at the surface which would render penetration by the reacting liquid difficult. The same objection may be raised in respect to further experiments devised to ascertain whether the extent of the fixation of sulphur was influenced by the concentration of the sulphur chloride. Very dilute solutions were employed, the concentration ranging from 0.0125 gr. to 0.1 gr. sulphur chloride per 100 c.c. of petroleum ether. Equilibrium was taken as being established at the end of two hours, and the samples were then withdrawn and the sulphur contents determined. The amount of sulphur fixed was shown to be dependent on the concentrations, and not on the absolute quantities of the sulphur chloride present, and the relative amounts of sulphur taken up at different concentrations were generally in accord with the adsorption equation. The assumption was made that equilibrium was established at the end of two hours, which, for the very low concentrations employed, may not be valid.

Even though the sulphur chloride is regarded as entering into combination with the rubber, the effect of vulcanisation may well be the result of an adsorption of this additive compound at the moment of formation by the unchanged rubber, just as has been assumed to be the case with rubber vulcanised by means of sulphur.

#### OTHER VULCANISING AGENTS

Vulcanised rubber which can be regarded as satisfactory from the point of view of mechanical properties has so far been obtained only by a process

\* *Koll. Zeit.*, 1910, 6, 281.

involving the use of sulphur or sulphur chloride. From time to time, however, other agents have been found capable of imparting to the rubber properties which in some measure resemble those possessed after vulcanisation by the methods commonly employed.

In some instances the effect obtained is merely a surface phenomenon due to formation of a derivative, as in the case of the halogens and certain hypochlorites which have frequently been proposed. The effect is confined to the removal of tackiness, and the mechanical properties are not visibly improved.

Antimony iodide was proposed by Fawsitt \* as being especially suited for vulcanisation by the dry heat process (p. 205), but the method has never found commercial application.

From a consideration of the fact that both sulphur and sulphur chloride possessed the property of reacting with unsaturated hydrocarbons, Ostromisslenski concluded that other substances which reacted similarly should be capable of promoting vulcanisation.

As certain organic nitro-derivatives exhibit this behaviour, attempts were made to vulcanise rubber employing compounds of this type. It was found that even in the absence of sulphur the phenomenon of vulcanisation was evident on heating mixtures of rubber containing certain metallic oxides, notably magnesium oxide and litharge, with such compounds as 1 : 3 : 5-trinitrobenzene, mononitrobenzene, tetranitronaphthalene, and picryl chloride.

Certain other substances, such as triphenylmethane, which are known to form addition compounds with unsaturated hydrocarbons, did not, however, cause vulcanisation to take place, and it was thought that the action might be due to the oxidising influence of the nitro-groups. Ostromisslenski, therefore, considered that other oxidising agents would give similar results, and the experiments were extended to include organic peroxides. Benzoyl peroxide was found to be extremely active, heating for only five minutes at 114° C. giving a product described as completely vulcanised; no effect was produced by substituting barium peroxide for the benzoyl peroxide.

The published data did not give any indication of the tensile properties of the vulcanised material, the disappearance of tackiness being regarded as the criterion, and the samples were described merely as being either completely or incompletely vulcanised.

The results, however, have been confirmed by Stevens,† who has examined the properties of the vulcanisates obtained by employing *m*-dinitrobenzene and 1 : 3 : 5-trinitrobenzene in place of sulphur. A mixture of 100 parts of

\* *J. S. C. I.*, 1892, 11, 332.

† *Ibid.*, 1917, 36, 107.

rubber with 8 parts of litharge was taken as the basis for incorporating varying proportions of the nitro-derivatives.

After a period of heating of only five minutes at  $135^{\circ}$  C. the mixture containing 4 parts of trinitrobenzene gave a breaking load of 0.954 ki. per sq. mm., the length at break being 8.56 times that of the original sample. These results, while being decidedly inferior to those obtained from mixings containing sulphur (see p. 135), are nevertheless indicative of a marked vulcanisation effect.

It is interesting to note that the compounds behave somewhat similarly to sulphur in that a proportion appears to be fixed by the rubber; in the case of sym. trinitrobenzene originally present to the extent of 1 per cent., the acetone extract of the "vulcanised" sample did not contain any of the substance, as indicated by the absence of red coloration on adding alkali. Where larger proportions than 1 per cent. of the nitro-compound were employed the reaction was obtained. Determinations of nitrogen in the acetone extract also showed that some of the nitro-compound had been retained by the rubber.

Products with fairly good tensile properties were also obtained by employing magnesia instead of litharge. A mixing containing 100 parts rubber, 30 parts magnesia and 4 parts of sym. trinitrobenzene vulcanised for forty minutes at  $140^{\circ}$  C. gave a product with a breaking load of 1.06 ki. per sq. mm., the length at break being 5.42 (original = 1.0).

According to Ostromisslenski, vulcanisation can be induced by trinitrobenzene even in the absence of inorganic oxides, but Stevens was unable to confirm this statement; Bunschoten\* also states that metallic oxides must be used in conjunction with nitro-compounds in order to ensure that vulcanisation shall take place.

In experiments with benzoyl peroxide Stevens found that although the characteristics of vulcanisation were imparted to the rubber, the tensile properties of the products were not of a very high order, comparing unfavourably with those resulting from the use of trinitrobenzene.

Although these organic vulcanising agents do not at present possess any technical interest, since the mechanical properties of the products are not of the same order as those obtained by the aid of sulphur, there is a possibility that further investigation may result in the discovery of methods of application by which the properties will be greatly enhanced.

From a purely scientific point of view a study of the changes brought about by organic compounds of various types may afford a clearer insight into the phenomenon of vulcanisation. If a substance incapable of reacting with

\* *Chem. Weekblad*, 1918, 15, 257.

rubber could be found which would produce the effect known as vulcanisation, the physical nature of the process would be established. Even in the case of the nitro-compounds examined by Ostromisslenski the possibility of a chemical reaction is not altogether excluded.

From the analogy between selenium and sulphur it might be expected that the behaviour towards rubber in the case of selenium would be similar to that of sulphur. Patents have been taken out from time to time \* claiming the use of selenium, but very little experimental data is available regarding the effect produced. An investigation by Boggs † showed that the black modification, if incorporated with rubber containing an organic accelerator, preferably an organic amine, ‡ gave a product possessing tensile properties very little inferior to those resulting from the use of sulphur. The time of heating necessary was, however, twice as great as when sulphur was employed.

\* Cf. Pearson, *Crude Rubber and Compounding Ingredients*.

† *J. I. E. C.*, 1918, 10, 117.

‡ U.S. Pat. 1364055.

## CHAPTER IX

### PROPERTIES OF VULCANISED RUBBER

#### PHYSICAL PROPERTIES

VULCANISED rubber, as has been stated previously (see p. 102), is insoluble or almost insoluble in all ordinary solvents for raw rubber. If it is heated to comparatively high temperatures, 180 to 200° C., for a long time disintegration takes place and a homogeneous solution is obtained; the rubber which is obtained on reprecipitation with acetone is, however, very much reduced in strength, and the passage into solution is obviously accompanied by a process of degradation.

The swelling observed when vulcanised rubber is immersed in organic liquids is much less pronounced than in the case of unvulcanised rubber.

The change in the swelling capacity of rubber with increasing degree of vulcanisation has been investigated by Kirchhof,\* who employed a mixture of 100 parts Plantation Para rubber and 12.5 parts of sulphur. This was heated for varying times to give a series of products having vulcanisation coefficients of 1.2, 2.0, 3.5, 4.4 and 6.4 respectively. Discs 1 mm. thick were immersed in different solvents, including light petroleum, benzene, carbon disulphide and carbon tetrachloride, and the amount of liquid taken up in a given time determined by weighing.

According to Kirchhof, the swelling reaches a maximum in twenty-four hours, although the writer's experience is that a much longer time is necessary for the completion of the process.

As in the case of raw rubber, different liquids have different swelling powers for the same sample of rubber, the quantity of liquid taken up at maximum swelling being an exponential function of the specific gravity.

The maximum swelling with a particular liquid decreases as the coefficient of vulcanisation of the rubber increases, and Kirchhoff deduces the following quantitative relationship.

$$Q_v \cdot K^e = k \text{ (constant),}$$

where  $Q_v$  (Quellung) is the volume percentage of swelling medium taken up,

\* *Kolloidchem. Beihefte*, 1914, 6, 1.

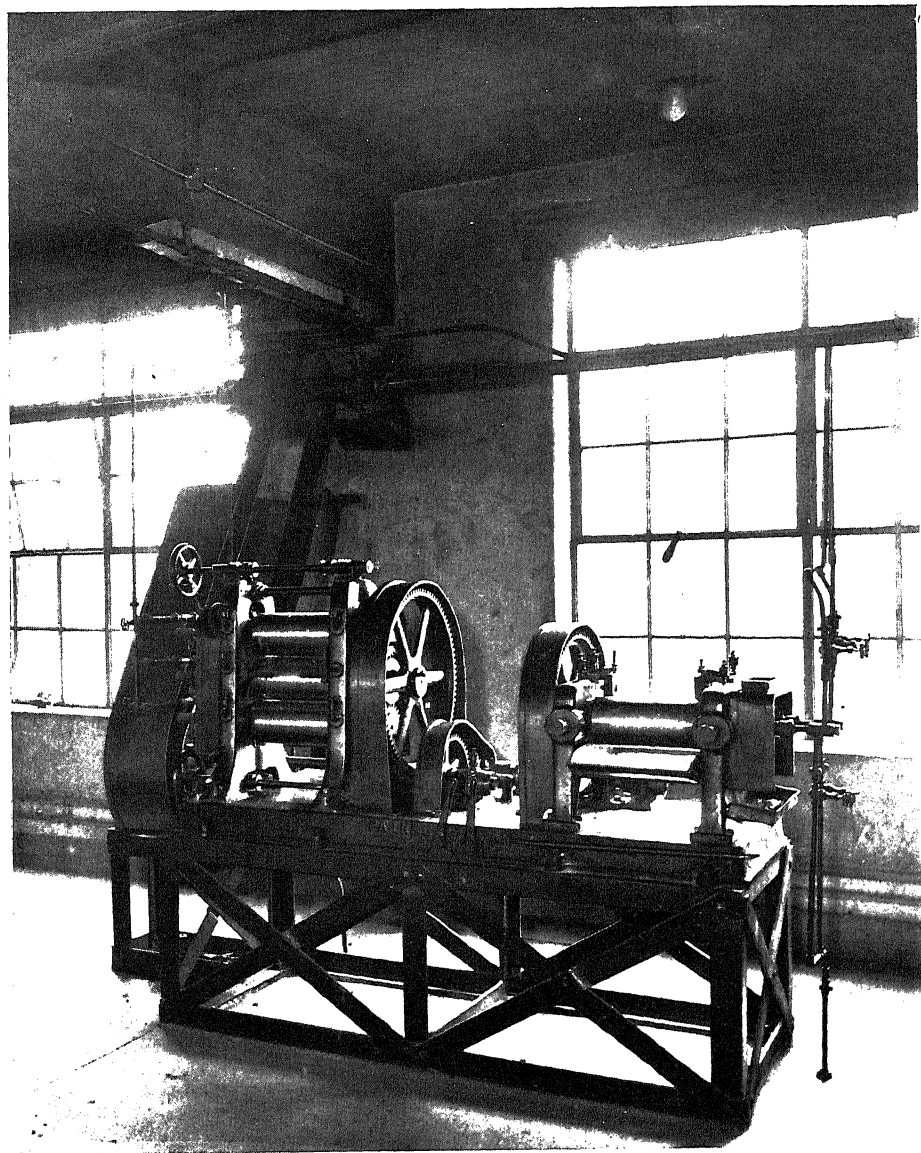


PLATE 9.—EXPERIMENTAL MILL AND CALENDER.



$K$  is the vulcanisation coefficient and  $\epsilon$  is an exponent which depends upon the nature of the swelling medium. At maximum swelling the values of  $k$  and  $\epsilon$  for different media are benzene  $k1386$ ,  $\epsilon0.645$ ; carbon disulphide,  $k1590$ ,  $\epsilon0.71$ ; carbon tetrachloride,  $k3490$ ,  $\epsilon1.016$ .

While this may be true of a particular mixture of rubber and sulphur, it is unlikely that the equation is of general application, as the swelling power of a sample of vulcanised rubber will be affected by the presence of inorganic constituents.

It is more likely that there exists a definite relationship between the tensile properties and the swelling properties of vulcanised rubber, but as the tensile properties of samples having the same coefficient of vulcanisation are not always identical, the correlation between the coefficient of vulcanisation and the maximum swelling capacity may not always hold good.

It may indeed be found possible to apply the method of swelling to the examination of the tensile properties of samples which are too small to admit of handling in the usual testing machines.

When rubber is exposed to the vapour of the liquid, swelling takes place to a much smaller extent than when the sample is immersed in the liquid, and in this case the swelling maximum appears to be independent of the degree of vulcanisation.

An investigation of the swelling of vulcanised rubber in petrol was undertaken by Dubosc,\* who employed strips of rubber taken from motor tyres, apparently with the object of determining the extent to which these might be affected by coming into contact adventitiously with the swelling liquid. An interesting feature of his experiments was the extremely long period which elapsed before swelling reached a maximum.

An attempt to correlate the swelling power with some other physical property of the swelling medium has been made by Ostwald,† who, from an examination of the results obtained by Flusin‡ and Posnjak,§ concludes that the swelling power decreases with increasing di-electric constant of the liquid.

### TENSILE PROPERTIES

Since vulcanisation is carried out industrially for the purpose of imparting certain physical or mechanical properties to the rubber, it is clear that in the evaluation of vulcanised rubber the physical and mechanical characteristics must be taken as criteria.

Rubber is, however, adapted to the manufacture of articles differing widely

\* *Le Caout. et la G. P.*, 1919, 16, 9781.

† *Ann. Chem. Phys.*, 1908, 13, 488.

‡ *Koll. Zeit.*, 1921, 29, 100.

§ *Kolloidchem. Beihefte*, 1912, 3, 417.

in character, and it is not possible to specify a particular property which it is desirable should be possessed by rubber for whatever purpose it is to be applied.

Nevertheless, in the majority of cases a study of the tensile properties affords an indication of the suitability of the rubber for a particular purpose.

Reference has already been made to the progressive nature of the chemical changes accompanying vulcanisation. Similarly, the tensile properties of the rubber undergo a gradual transformation, and these may be followed by an examination of the stress-strain relationships.

The tests are usually carried out with the aid of an apparatus designed to operate upon test-pieces of suitable shape and dimensions; two main types are in use, one adapted for straight, the other for ring-shaped test-pieces.

In cases where a straight test-piece is to be employed, the rubber is incorporated with the sulphur in the usual manner (see p. 200) and vulcanised in a mould to give a sheet of a definite thickness. From this sheet there is punched out by means of a die a strip of rubber with widened ends, usually referred to as a "dumb-bell"-shaped test-piece.

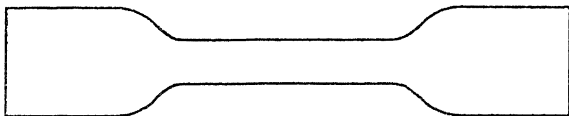


FIG. 2.

This particular shape is chosen because when a straight test-piece having the same width throughout is secured at each end by grips and stretched, the part at the grips would tend to elongate in the same manner as the rest of the piece, and would therefore be liable to slip away from the grips, and perhaps break at this point. When the ends are wider and consequently present a larger cross-sectional area, the elongation in this portion of the sample is not so marked as in the narrower portion. This central section of the test-piece is the part upon which stress-strain data are obtained. A definite length is marked off by means of ink, and gradually increasing loads are applied to the test-piece up to the breaking point, the distance between the marks corresponding to each load being noted. The loads are usually indicated on a dial, the whole apparatus working on the principle of the spring balance. The loads (stresses) expressed in kilograms per square millimetre or other suitable units are plotted against elongation (strains) expressed in percentages of the original length, and the stress-strain curve is thus obtained.

While an apparatus of this type gives satisfactory results, two operators are necessary to carry out a test, one to take note of the loads and the other to record elongations.

The testing machine which is more frequently employed is of the type devised by Schopper, which is arranged to operate with ring-shaped test-pieces. This is shown in Plate 12.

In this case the sample is vulcanised as before to give a sheet 5 mm. thick from which a ring of 44.6 mm. internal and 52.6 mm. external diameter is punched out with the aid of a die or cut by means of two rotating knives set at different distances from a central shaft; cutting is facilitated by wetting the knife with soap solution.

In order to ensure accurate control of the time and temperature at which the rubber is vulcanised, an apparatus similar to that devised by Spence and Young (see p. 98) may be employed. A convenient modification has been described by Van Rossem,\* in which the bath of glycerine heated by xylene vapour is replaced by a bath of mineral lubricating oil of high flashpoint. The oil bath consists of a rectangular sheet-iron trough capable of holding 10 to 15 gallons of oil, which is heated by means of a ring gas-burner. With such a large bulk of oil it is a comparatively easy matter to keep the temperature correct to 0.2 to 0.4° C. without the aid of a thermo-regulator, but it is advisable to employ a mechanical stirrer to ensure a uniform temperature throughout. The mould in which the rubber is enclosed consists of two circular recessed plates fastened together with bolts provided with winged nuts; the recess is exactly 5 mm. in depth and at least 75 mm. in diameter, and a channel is provided at the edge of the disc. If desired, a double mould, such as is recommended by Twiss and Brazier, may be employed; in this way each mould will give two discs vulcanised under the same conditions from which rings may be cut for obtaining duplicate tests.

The amount of rubber taken is such that the mould is not completely filled, but is sufficient to give a disc from which a ring of the required diameter may be cut.

Before closing the mould a few drops of water are poured into the channel, and thus during vulcanisation the internal pressure is equivalent to that of the steam at the temperature employed.

In place of the grips in the machine previously described, the ring is passed over two pulleys placed vertically one above the other. The upper one is fixed to the short arm of a weighted lever, the lower pulley being connected to a movable rod arranged so that when it is set in motion the pulley is rotated. When the ring is in position the rod is set in motion and tension is applied gradually to the ring, which is kept rotating by the movement of the lower pulley. In this way the tension is equally distributed throughout the test

\* *Delft Comm.*, 5, 139; cf. Twiss and Brazier, *I. R. J.*, 1921, 62, 25.

specimen. As the tension is applied the rubber ring is gradually extended, the load applied being indicated by the degree of inclination of the long arm of the lever, which at the commencement of the test is at rest in a vertical position.

The machine is usually provided with an autographic arrangement which records the loads and elongations on a chart carried by a drum. The recording pen is moved vertically to correspond proportionally with the elongation of the ring, and at the same time the moving lever imparts a rotary movement to the drum. In this way the loads and elongations are recorded on squared paper, and there is therefore no necessity to take readings at intervals.

In the Schopper machine the movements of the drum and pen are arranged in such a way that a displacement of 1 mm. on the vertical scale corresponds to 3.5 mm. extension, or 5 per cent. calculated on 70 mm., one half of the inner circumference of the ring employed. Horizontally a rotation of the drum giving a movement of 1 mm. at the circumference corresponds to 0.4 kg. load.

The width of the ring is 4 mm. and the thickness 5 mm., giving a cross-sectional area of 20 sq. mm., but as both halves of the ring are equally under tension, the total cross-sectional area tested is 40 sq. mm. Thus a rotation of 1 mm. corresponds to 0.4 kg. per 40 sq. mm., or 0.01 kg. per sq. mm.

As the records obtained are based on the use of a ring of exactly 140 mm. inner circumference and a cross-sectional area of 20 sq. mm., direct measurements from the autographically recorded stress-strain curve are correct only if the dimensions specified have been adhered to; if this is not the case, corrections must be made.

The stress-strain curves obtained in this way indicate the load per unit cross-sectional area necessary to break the sample and also the elongation at any load up to the breaking point. The load required to break the sample, usually expressed in kg. per sq. mm. of original cross-sectional area, less frequently in lbs. per sq. in., is variously described as the "tensile strength," "breaking load," "breaking stress" and sometimes as "breaking strain." The elongation is generally expressed as a percentage, sometimes as a multiple of the original length. Frequently the change in length is reported not in terms of elongation, but in terms of the ratio which the final length bears to the original; thus an elongation of, say, 800 per cent. is sometimes expressed as a final length of 900 per cent. of that of the original sample.

Although the Schopper type of machine is almost exclusively employed in the various official testing stations and research institutes in this country and on the Continent, and by workers in the rubber-growing countries, a machine employing straight test-pieces is more frequently adopted in America. Objection has been raised against the ring test-piece on account of the fact

that the values obtained are not sufficiently accurate owing to the uneven distribution of the stress over the cross-sectional area.\* This arises from the difference between the inner and outer circumferences of the ring, the inner diameter, on which the measurement is based, being 8 mm. less than the outer one, consequently the elongation of the outer circumference is not as great proportionally as the elongation of the inner one.

While this is true, the error introduced in this way is not of great magnitude with rings of small thickness, and in any case the results obtained will be comparable *inter se*.

In carrying out mechanical tests it is important to allow the rubber to remain at rest for a definite period, say twenty-four hours, after vulcanisation; as will be shown later, the tensile properties alter during storage, and therefore, when accurate comparisons are to be made, the test-pieces must be examined at the same stage in this ageing period. Further, tests should be carried out at a fixed temperature, as Wormeley † has shown that with increasing temperature the tensile strength decreases and the ultimate elongation increases.

The alteration in tensile properties of rubber on vulcanisation is illustrated in Fig. 3, which gives the stress-strain curves obtained from a mixture of 90 parts by weight of anaërobic rubber and 10 parts by weight of sulphur after heating for varying periods at 140° C.

In the first place, it will be noticed that the general form of the curve differs entirely from that given by metals. In the case of rubber the elongation increases rapidly for comparatively small increases of load until a point is reached at which the curve changes sharply in direction, and the application of further loads effects comparatively small increases in the elongation. It will be seen on comparing the various curves that shortly after the point of inflexion is passed the curve becomes rectilinear in form and the lines are approximately parallel. In the case of mixings made up with rubber and sulphur only, the inclination of this upper portion of the curve to the horizontal axis was proposed by Schidrowitz and Goldsborough ‡ as an index of the quality of the rubber employed.

The higher the quality of the rubber the less will be the inclination or "slope" of the curve, or, in other words, the less will be the extension observed on applying an additional standard load to rubber already stretched. Obviously the actual inclination of the upper portion of the curve will depend on the scale adopted for the ordinates and abscissæ, so that, unless standard scales are employed, the slope cannot well be expressed in terms of the angle of

\* U.S. Bureau of Standards, Circular 38, 1921, p. 66. † Rubber Industry, 1914, p. 246.

‡ I. R. J., 1916, 51, 505; J. S. C. I., 1919, 38, 347 T.

inclination. A more easily comparable standard is found by expressing the "slope" in terms of the elongation produced by a standard increment of load at high elongation. Schidrowitz and Goldsborough take as their unit the increase in elongation which takes place on increasing the load from 0.6 kg. per sq. mm. to 1.04 kg. per sq. mm., the figure thus obtained being

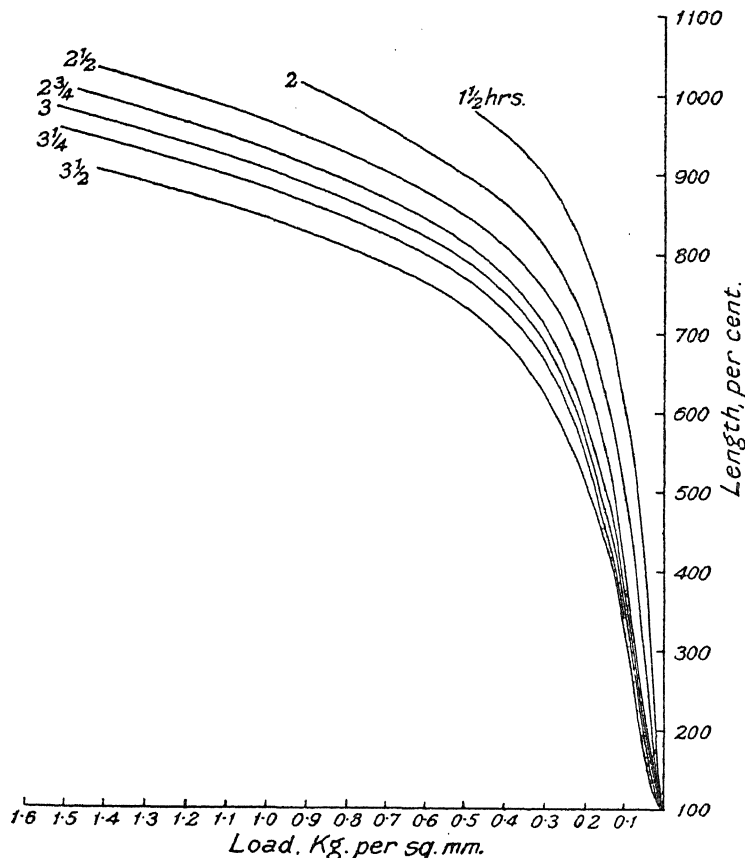


FIG. 3.

divided by 2.5. Thus the "slope" or "type" of the curve is derived from the expression

$$T = \frac{E_1 - E}{2.5}.$$

where  $T$  = "type" or "slope,"

$E$  = elongation in percentage of the original length at a load of 0.6 kg. per sq. mm.

$E_1$  = elongation in percentage of the original length at a load of 1.04 kg. per sq. mm.

The two points are arbitrarily chosen, but are probably taken as falling well within the linear portion of the curve.

According to Schidrowitz and Goldsborough, the slope of the curve is typical of a particular sample of rubber, and is independent of the state of the cure, as the lines derived from increasing times of cures are parallel; hence the slope is often referred to as the "type" of the rubber. It has been pointed out by de Vries \* that the curves are not strictly parallel, as an examination of the publications of various workers, including those of Schidrowitz and Goldsborough (*loc. cit.*), will show; nevertheless, although the "slope" may not be the same for all times of cure of the same rubber, a knowledge of this characteristic affords a very good basis for comparing the tensile properties of different lots of rubber.

Now, as the tensile properties of the rubber undergo a progressive change during vulcanisation, it is important to know at what point these properties are such that the best results would be obtained in a manufactured article. An inspection of the curves resulting from periodical tests of a particular mixing during vulcanisation (Fig. 3) shows that in the early stages of heating the rubber is rapidly extended with small increases of load, until shortly after passing the point of inflexion the sample breaks as indicated by the cessation of the curve. With increasing times of heating the curve becomes longer, and its course lies within that of the preceding one; this is more noticeable in the upper portion, which comes gradually nearer to the horizontal load axis, the earlier or vertical portion undergoing less displacement. This is equivalent to saying that the progressive effect of vulcanisation is to yield a product with increasing breaking load and possessing increasing resistance to stretching at high elongations. On further heating, however, the curve becomes shorter once more, although the flat portion continues to approach the horizontal axis.

### VARIATIONS IN THE PROPORTION OF SULPHUR

Hitherto consideration has been given to the tensile properties of vulcanised rubber-sulphur mixtures containing at least  $7\frac{1}{2}$  per cent. of sulphur, in which case vulcanisation at temperatures in the neighbourhood of  $140^{\circ}$  C. produces a progressive change in the position of the stress-strain curve. With lower percentages of sulphur the movement of the curve may be arrested, and indeed may be succeeded by a reversal of the direction as the heating period is extended. This has been already shown by de Vries and Hellendoorn \* in the case of rubber-sulphur mixings containing 5 per cent. of sulphur. A comparison of the behaviour of such a mixing with a  $7\frac{1}{2}$  per cent. mixing is shown in the

\* *J. S. C. I.*, 1920, 39, 310T.

following table, giving the tensile strength and length at a load of 1.20 kg. per sq. mm.:

Time of Vulcanisation.	Tensile strength kg. per sq. mm.		Length at 1.20 kg. original = 100.	
	7½% S.	5% S.	7½% S.	5% S.
75 . . . . .	1.33	—	991	—
90 . . . . .	1.31	1.19	960	1159
105 . . . . .	1.15	1.22	913 *	1122
120 . . . . .	0.71	1.35	870 *	1101
135 . . . . .	—	1.27		1095
150 . . . . .	0.17	1.31		1089
180 . . . . .	—	1.20		1109
240 . . . . .	0.15	1.09		1139

\* By extrapolation.

As the time of heating increases, the 7½ per cent. mixing which had already attained maximum tensile strength at 77 minutes gradually becomes weaker at first and then rapidly deteriorates at 150 minutes, breaking at only 0.17 kg. per sq. mm.; the 5 per cent. mixing gradually becomes stronger until at 120 minutes the maximum of 1.35 kg. is reached, when the decline sets in, but even at 240 minutes the sample is still comparatively strong.

With respect to tensile strength the changes are of the same character in both samples, although the loss of strength is much more rapid in the case of the 7½ per cent. sample. The length at a load of 1.20 kg. per sq. mm. is an indication of the position of the upper portion of the stress-strain curve, and alterations in the length serve to illustrate the movement which the curve as a whole would exhibit. The mixing with 7½ per cent. sulphur shows a progressive diminution in the length at this load, that is to say, the curve moves slowly towards the load axis. On the other hand, the 5 per cent. sulphur mixing shows a gradual diminution in length until at a cure of 150 minutes the value attains a minimum; after further heating the length increases once more, until at 240 minutes the length is greater than that at 105 minutes. In other words, the stress-strain curve has moved upwards once more and attained a position at 240 minutes' cure similar to that occupied at a cure of less than 105 minutes. Thus the same stress-strain curve represents two entirely different states of cure. This phenomenon of "reversion" is assumed to be



due to the exhaustion of the free sulphur at the stage where the curve is arrested; from then onwards the softening effect of heat is no longer counter-balanced by the pectising or stiffening effect due to the sulphur, the result being as indicated. Further examples of reversion have been quoted by Schidrowitz and Goldsborough,\* who point out that under certain conditions, as in the presence of mineral accelerators, not only the direction, but also the character of the curve may alter on continued vulcanising; this aspect of the question will be treated more fully in a succeeding chapter.

### OTHER MECHANICAL TESTS

Apart from the purely tensile tests, it is sometimes necessary to examine the mechanical properties of rubber from other points of view, according to the particular use to which the article is to be put. Consideration will here be confined to those properties which will be subsequently referred to in connection with the influence of different modes of treatment on the resulting rubber.

*Measurement of "Set."*—When a vulcanised rubber is stretched and the tension released, it will be found that the original dimensions are not attained, but that an extension in length in the direction of the stretch has taken place. If the sample is allowed to remain undisturbed it will be found that a gradual shrinkage in length will occur, but that ultimately this will stop even though the sample has not returned to its original dimensions. The elongation which the sample has undergone is referred to as the "permanent set," and in a particular mixing this set will be reduced in magnitude as vulcanisation proceeds; thus, in the early stages of vulcanisation, as with raw rubber itself, the set may be comparatively high, whereas when vulcanisation has been carried further there will be a much less pronounced deformation. It may not always be convenient to wait until the sample has reached a state of equilibrium, in which case the measurement may be made after the lapse of a definite period from the time when the tension is released; in this case the deformation is referred to as the "sub-permanent set." The tension may be applied in the form of a definite load per unit cross-sectional area, or the sample may be stretched to give a definite elongation. King and Cogswell † prefer the latter method as likely to yield more consistent results; these authors recommend a period of twenty minutes for the application of the stress, and a recovery period of five hours or less before the actual measurements of "set" are made. Frequently the set is measured after breaking, using the sample employed for the tensile tests.

\* I. R. J., 1919, 67, 269.

† *Ibid.*, 1922, 63, 30.

*Hysteresis.\**—It has been shown that the increasing application of stress to a sample of vulcanised rubber produces a progressive elongation, and that by plotting the values for the stress and strain a characteristic curve is obtained. The area enclosed by the stress-strain curve and the elongation axis represents the energy absorbed during expansion. When the tension is released and the rubber is allowed to retract the curve follows a different course from that produced during extension, and the area enclosed is smaller than that enclosed

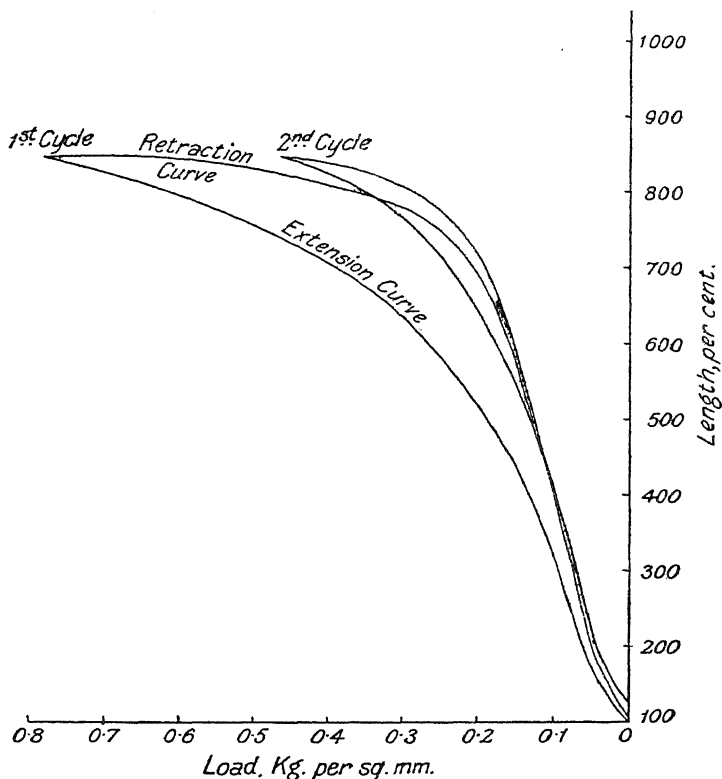


FIG. 4.

by the extension curve. Thus the energy given out on retraction is less than that absorbed on extension, and this loss or hysteresis will be indicated by the difference in the areas enclosed by the two curves. In comparing the hysteresis of different samples they may be stretched by means of a given load per unit area of cross section or extended to a definite percentage elongation. Typical curves showing the hysteresis loops after extending to 750 per cent. elongation

\* For a description of a machine and of methods for obtaining data regarding hysteresis, see Schwartz, *I. R. J.*, 1910, 38, 106, 147, 278, 341, 425, 483; 1910, 39, 376; also Wiegand, *J. I. E. C.*, 1921, 13, 118; Evans, *I. R. W.*, 1921, 65, 192.

are given in Fig. 4, which shows the results of two consecutive cycles of extension and retraction. It will be observed that the loss in the first cycle is much greater than in the second, and successive cycles would give loops almost coinciding with the second. In carrying out hysteresis tests, standard methods must be adhered to, as the nature of the curves will be influenced by such factors as the rate of application and releasing of stress, the time of rest allowed between each successive cycle, and the length to which the sample is extended.

*Other Tests.*—In some cases other tests may be required, as, for example, the resistance to abrasion. This may be arrived at either by fixing the sample against a revolving abrasive wheel and noting the loss in volume or weight per unit time, or the sample may be introduced into a rotating barrel filled with some abrasive material, such as sand. Hardness tests are sometimes desirable, in which case use may be made of one of the forms of Plastometer.\*

### DETERMINATION OF CORRECT CURE

In the early days of the testing of rubber the attainment of maximum breaking load was taken as criterion of correct vulcanisation. Eaton and Grantham † have pointed out that at the point of maximum breaking load the extensibility of the rubber is sometimes low and the rubber is obviously "over-vulcanised." They adopt as criterion the "optimum cure," which is the point where the product of the length at break and the breaking load is a maximum. The value arrived at in this way, sometimes called the "tensile product," is practically equivalent to the load at break expressed in terms of the cross-sectional area at break, instead of in terms of the original area. This is strictly true only if the area of the cross section at a given length is inversely proportional to the total length, which would be the case if there were no change in total volume on stretching rubber. While there may be considerable volume changes in rubber mixings containing certain compounding ingredients (see p. 168), the inverse relationship between area and elongation in a stretched sample containing only rubber and sulphur holds good. In the majority of cases it will be found that the time of heating which gives the product with the maximum breaking load is the one which gives the maximum "tensile product," so that only in exceptional cases does it happen that the "optimum cure" differs from the cure giving maximum tensile strength.

Other workers have adopted different standards for the comparison of raw rubbers. For example, de Vries and Hellendoorn ‡ vulcanise a mixture

\* Gurney, *I. R. W.*, 1919, 61, 140.

† *J. S. C. I.*, 1915, 34, 990.

‡ *Archief*, 1918, 2, 785.

of  $92\frac{1}{2}$  parts rubber and  $7\frac{1}{2}$  parts sulphur at  $148^{\circ}$  C. until a load of 1.30 kg. per sq. mm. produces an elongation of 890 per cent. (*i. e.* a total length of 990 per cent. of the original); the standard stress-strain curve will be that which passes through this point.

Methods such as these are useful chiefly for the purpose of examining various raw rubbers, but the figures cannot be taken as absolute, since the composition of rubber articles varies considerably, and only in special instances are mixtures of rubber and sulphur alone employed; apart from this, the proportion of sulphur to rubber varies with different mixings and is infrequently of the order employed in these tests. Nevertheless the results obtained are valuable in that they afford a means of comparing the rate of cure and tensile strength of one consignment of rubber with the standard.

#### AGEING

Although the cure giving rubber possessing maximum tensile properties might be thought the most suitable for adoption in works practice, it is important to know whether this maximum strength will persist for a considerable time after the article has been manufactured.

Stevens \* indeed showed that rubber vulcanised to give the maximum tensile product was extremely liable to deterioration on keeping for some months. A mixing of 90 parts of pale crêpe rubber and 10 parts of sulphur was vulcanised at  $134.5^{\circ}$  C. for periods varying from two hours to four and a half hours, and the samples stored at normal temperature in the dark. Tests were carried out at intervals up to 311 days, the results obtained being as shown in Table X, p. 127.

It will be noticed that in every instance the sample giving the highest breaking load is the one giving the highest tensile product, and therefore the "optimum cure" is here the same as the cure giving maximum tensile strength. At the beginning of the test the sample vulcanised for four and a half hours exhibited maximum tensile properties, but after keeping for the full period these were almost entirely lost. The deterioration in the case of the sample cured for four hours was not so marked, while that cured for three and a half hours had deteriorated still less. The sample giving the maximum tensile product at the end of the "ageing" period is the one cured for three hours, which at the time of manufacture was not equal in strength to those cured for longer periods.

These experiments were carried out at normal temperatures prevailing at the time, and in a later series Stevens † showed that the effect of ageing in an

\* *J. S. C. I.*, 1916, 35, 872.

† *Ibid.*, 1918, 37, 281 T.

TABLE XI  
PALE CRÊPE.

	Age in days.	Cure (hours).					
		2	2½	3	3½	4	4½
Breaking load (gms. per sq. mm.) . . . . .	4	960	1230	1510	1690	2010	2480
	125	950	1550	1610	1930	1760	1760
	203	1010	1500	1630	1740	1480	490
	311	920	1400	1640	1480	1330	170
Final length (original length = 100) . . . . .	4	1151	1098	1078	1013	987	953
	125	1016	1017	991	952	897	851
	203	1042	1032	1004	936	858	611
	311	1035	1009	993	894	822	372
Tensile product . . . . .	4	110	136	162	170	199	236
	125	93	153	159	183	158	150
	203	105	155	163	163	127	30
	311	95	141	163	132	109	6
Coefficient of vulcanisation		2.0	2.6	3.2	4.1	4.5	5.0

incubator kept at 28° C. was much more marked than at a temperature of 10.5° C. The degree to which deterioration takes place is also dependent on the humidity of the atmosphere, Stevens \* having shown that rubber may be kept in air saturated with moisture even at tropical temperature for a period of six months without appreciable loss of strength. It is pointed out that ageing experiments carried out in this country may yield results differing from those obtained in tropical countries.

As the results of Stevens indicate, ageing is accompanied by an alteration in tensile properties, the character of which is influenced by the state of cure of the sample under test.

De Vries and Hellendoorn,† in the course of experiments on the ageing of vulcanised rubber at tropical temperatures, about 27° C., have shown that as ageing progresses the stress-strain curve moves gradually towards the load axis, that is to say, down the paper if the curve is plotted as described in Fig. 3, indicating that the rubber becomes less extensible for a given load. At first there is a slight increase in tensile strength, succeeded by a gradual

\* J. S. C. I., 1920, 39, 251 T.

† I. R. J., 1921, 61, 87.

falling off, so that the curve lengthens in the early stages and then becomes shorter. The period over which this increase in tensile strength takes place is longer in cases where the sample is comparatively in a less advanced state of cure. In the case of a mixture of rubber and sulphur in the proportion of  $92\frac{1}{2}$  and  $7\frac{1}{2}$ , vulcanised for 90 minutes at  $148^{\circ}$  C., after two and a half years the tensile strength was still higher than at the beginning of the test, whereas with a similar mixture vulcanised for 125 minutes, the tensile strength had fallen from over 1.3 to approximately 0.9 kg. per sq. mm.

The alteration in chemical composition of rubber during ageing has been studied by Eaton and Day,\* who employed a mixing of rubber and sulphur (90 : 10) vulcanised for varying periods. The samples were exposed in the form of discs, and also after grinding to a fine "crumb," which was stored both on a watch-glass and in a specimen tube. In the case of the sample cured for nine hours an increase in weight of 39.4 per cent. was noted after nine months with the crumb stored in a tube, the increase of the watch-glass stored sample being only 25 per cent.; the rate of increase in weight was at first greater in the case of the sample kept on a watch-glass, but even the tube-stored sample increased more rapidly. The sample which was not crumbed, but kept in the form of a disc, increased to the extent of only 0.8 per cent. during this period.

This was thought to be due to processes involving the formation of some volatile compound which would escape more readily in the case of the sample freely exposed to air, as on a watch-glass.

The increase in weight was also very marked in the case of the sample cured for three hours, but that vulcanised for one and a quarter hours, which was close to the "optimum cure," increased to the extent of only 3.6 per cent. when stored in a tube and 6.0 per cent. when exposed on a watch-glass.

These results emphasise the fact that vulcanisation beyond a certain point yields a product which is relatively unstable and is liable to undergo chemical degradation as well as physical deterioration.

During the "ageing" of these samples it was noted that a considerable increase in weight was accompanied by the formation of water-soluble material which contained sulphur and possessed an acid reaction; thus the sample cured for nine hours gave an aqueous extract of 23.4 per cent., the acidity of which expressed as sulphuric acid corresponded to 2.68 per cent., and the total sulphur to 0.45 per cent., calculated on the original sample.

Somewhat similar results had been recorded by Stevens,† who noted that on keeping vulcanised rubber an increase in weight took place, and that at

\* *J. S. C. I.*, 1919, 38, 329 T.

† *Ibid.*, 1919, 38, 195 T.

the same time a volatile sulphur compound was formed; vulcanised rubber after acetone extraction was found to increase in weight much more rapidly than before extraction.

Both Stevens and Eaton and Day observed a slight increase in the coefficient of vulcanisation on ageing; this increase was the more marked the higher the coefficient at the beginning of the test.

On the other hand, de Vries \* has not observed changes in the value for the coefficient beyond the limits of experimental error.

### ACCELERATED AGEING

In view of the fact that an ageing test might well be expected to indicate the probable life of a particular vulcanised rubber, it is evident that the information obtained from such a test would be of more value to the manufacturer than a test based solely upon the tensile properties of the sample at the time of vulcanisation. In view of the length of time necessary for deterioration to occur at ordinary temperatures, "accelerated ageing" tests have been proposed in which the sample is stored under suitable conditions at an elevated temperature. The temperature chosen is such that vulcanisation will not proceed at a measurable rate, but high enough for reduction in strength to occur rapidly. For this purpose Geer † employed an oven through which air heated to 71° C. was passed, a number of samples of the mixing under examination being introduced and a proportion removed for tests every day. A somewhat similar method was adopted by de Vries, ‡ who worked with temperatures ranging between 65° and 75° C.

The apparatus employed by Geer and Evans has been fully described, § and consists of an oven or a series of ovens through which air previously heated to 71° C. is passed continuously. A large number of samples of the vulcanised rubber, cut to shape according to the testing machine to be used, are hung in the oven and three samples are withdrawn daily; these are allowed to remain at ordinary temperatures for twenty-four hours to attain a state of equilibrium and then tested in the ordinary way. In cases where only a small number of samples are under test an electrically controlled oven may be employed, provided that a continuous supply of air is allowed to pass through. A rapid decay of the samples is thus induced, but the results obtained are generally of the same character as those observed on ageing at ordinary temperatures. In the accelerated ageing test one day is equivalent to approximately six months of natural life.

\* *I. R. J.*, 1917, **53**, 102.

† *I. R. J.*, 1917, **53**, 101; 1919, **57**, 77.

‡ *I. R. W.*, 1916, **55**, 127.

§ *Ibid.*, 1921, **61**, 1163.

The stress-strain curve shows the same progressive movement towards the load axis as in the case of natural ageing, and as a rule there is an increase in tensile strength at the beginning of the test. The period over which this increase takes place varies according to the state of cure of the sample, and in some cases the decline may have set in by the time the sample is tested after one day of ageing, under which circumstances the initial increase, if it takes place, is not observed.

Thus the tensile characteristics of the rubber during ageing alter in the same manner as in ordinary hot vulcanisation, the breaking load increasing to a maximum and then decreasing, while the extensibility gradually decreases.

This progressive change in tensile properties is not accompanied by an increase in the proportion of combined sulphur commensurate with that which would be obtained if the same alteration were brought about by hot vulcanisation.

Thus de Vries (*loc. cit.*) found that a mixture of rubber and sulphur ( $92\frac{1}{2} : 7\frac{1}{2}$ ) vulcanised for 60 minutes at  $148^{\circ}$  C. increased in tensile strength from 0.71 kg. to 1.76 kg. per sq. mm. by keeping for 66 hours at  $70^{\circ}$  C., during which time the coefficient increased from 2.67 to 2.85. The tensile strength and extensibility of the sample at the end of the test were such that in order to reproduce these by hot vulcanisation a cure of 100 minutes was necessary, the coefficient of vulcanisation in this case being 4.40.

Typical results obtained on submitting to the accelerated ageing test rings made from a mixture of rubber and sulphur (90 : 10) vulcanised at  $142^{\circ}$  C. for varying periods are shown in Fig. 5.\* The breaking load of the sample is recorded daily, and it will be seen that in each case there is an initial increase followed by a more or less rapid decline. The vulcanisation coefficients are indicated against each sample, and it is clear that with the higher coefficients the loss of tensile strength takes place much more rapidly than with the lower coefficients. Sample D is obviously over-cured, since in four days the strength has fallen from over 1.2 to less than 0.3 kg. per sq. mm. Sample C, which was vulcanised to pass through the standard point adopted by de Vries,† preserves its strength for a much longer period, but is nevertheless somewhat over-cured. Sample B, with a coefficient of 3.15, exhibits satisfactory tensile properties over a longer range than the others; A may be regarded as under-cured. The irregularities in the curve indicate the unreliability of the figure for breaking load, which can be arrived at with any degree of certainty only by taking average figures from a large number of rings. The general trend of the curves is, however, apparent, and leaves little room for doubt as to which

\* Anderson and Ames, private communication.

† *Archief*, 1918, 2, 785.



is the most satisfactory sample. It is interesting to note that the sample vulcanised to give a curve passing through de Vries' point is somewhat over-cured. A mixing made up in the proportions employed by de Vries (rubber 92½, sulphur 7½) and cured at 142° C. until the curve passed through the same point was also found to be over-cured, a result which was in accordance with the opinion expressed by de Vries and Hellendoorn.\*

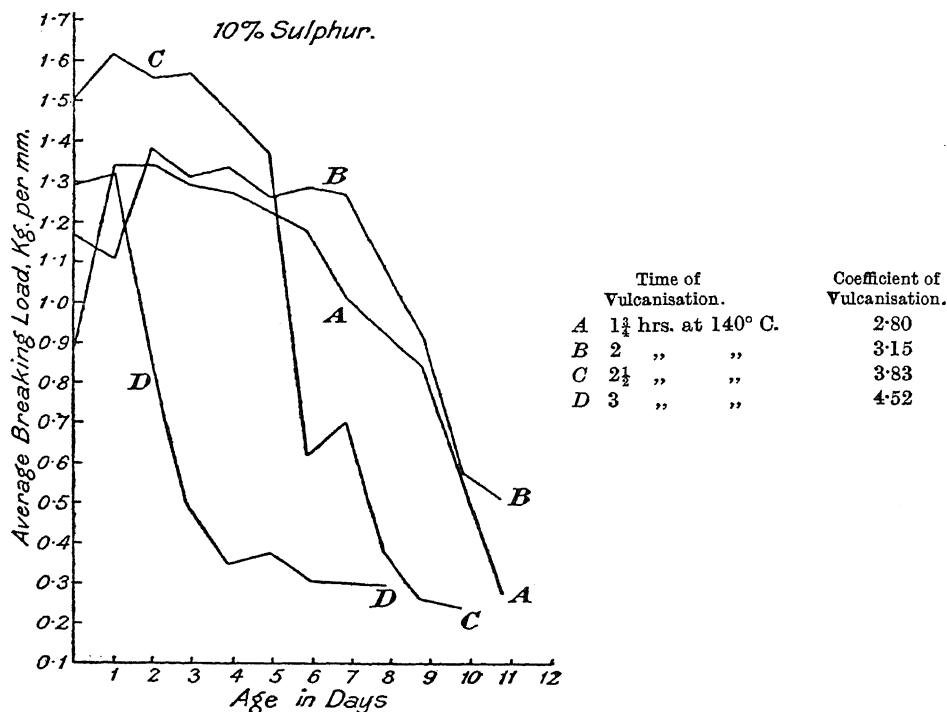


FIG. 5.

While there is in general a similarity between the phenomena accompanying natural and accelerated ageing, there is not yet sufficient evidence available to allow of an exact estimate being made of the probable life of a vulcanised rubber mixing as a result of such tests. It is possible, however, by this method to form an opinion as to the relative merits of a particular sample as compared with one which is known from experience to give satisfactory results.

It is interesting to note that Bruni † has been able to prove the formation of lævulinic aldehyde in a tube in which vulcanised rubber was exposed at a temperature of 77° C.; the same reaction was observed in the case of

\* I. R. J., 1921, 61, 88.

 † *Ibid.*, 1922, 63, 814.

vulcanised rubber which had "perished" at ordinary temperatures. This indicates a similarity between the processes of ageing at ordinary and at elevated temperatures.

### RELATIONSHIP BETWEEN CHEMICAL AND MECHANICAL PROPERTIES

It has already been explained that the process of vulcanisation is accompanied by a progressive change in both the chemical and physical properties of the rubber.

In order to decide at which stage of the process the rubber is "correctly cured" from a technical standpoint, it is necessary to know not only the tensile properties prevailing at the time of vulcanisation, but also for how long these properties will be retained, or at any rate whether deterioration will occur slowly or rapidly.

The question arises as to whether the state of cure of a sample of rubber should be ascertained by an examination of the tensile properties or by a determination of the coefficient of vulcanisation. From the results of ageing experiments Stevens came to the conclusion that the vulcanisation coefficient was a reliable index to the state of cure, since in cases where the value was approximately 3 the vulcanised rubber retained its tensile properties for a maximum period. On the other hand, Schidrowitz and Goldsborough \* had quoted instances in which the coefficient of vulcanisation of a number of samples all of which were regarded as "correctly cured" possessed coefficients ranging from 2.03 to 4.86.

Eaton and Day † found coefficients varying from 3.90 to 4.62 for samples vulcanised to give the "optimum cure," but in this case, as also in that cited by Schidrowitz and Goldsborough, the correct cure was based on the vulcanisate exhibiting maximum tensile properties at the time of vulcanisation, and not on an ageing test; all the samples were, however, probably at the same relative state of cure, and even if over-cured would be so to the same extent, in which case the differences in the coefficients would be of approximately the same order at the best cure from a technical point of view.

It is interesting to note that in general the samples vulcanised for the shortest time to give a correctly cured product possessed the highest vulcanisation coefficient.

Other instances have been cited by de Vries, ‡ who found the vulcanisation coefficient for samples of ordinary crêpe requiring different times of cure as follows :

\* *I. R. J.*, 1916, 51, 505.

† *J. S. C. I.*, 1917, 36, 1116.

‡ *J. I. E. C.*, 1921, 13, 1134.

TABLE XII.

Time of Cure.	Coefficient of Vulcanisation.
Mins.	
85	5.1
90	5.0
94	5.0
115	4.4
120	4.75
122.5	4.4

Thus, if the samples are arranged in order of increasing time of cure, the corresponding coefficients tend to show a gradual diminution.

Similarly, Martin and Elliott \* have shown that for a particular form of rubber, as the standard time of cure increases, so the vulcanisation coefficient at standard cure decreases, from which it may be concluded that the coefficient of vulcanisation does not always indicate the state of cure of a rubber-sulphur mixing.

So far consideration has been given only to simple mixtures of rubber and sulphur, and not to technical mixings, which generally contain other compounding ingredients. In an investigation extended to include mixings containing rubber 60, sulphur 3, and zinc oxide 37 parts by weight, Stevens † found that samples vulcanised to give a coefficient of 2-2.5, that is, appreciably lower than with a 90:10 rubber-sulphur mixing, gave the best results on ageing. Thus with the best cure as determined by ageing experiments, the coefficient varies according to the nature of the mixing. This has been further emphasised by a study of mixings containing organic accelerators, to which attention will be drawn later (see p. 184); it may here be said that in some cases a fully vulcanised rubber may be obtained with a coefficient of vulcanisation of 1.0 or less. It is, therefore, impossible to assign a definite value for a coefficient of vulcanisation which shall be applicable to all rubber mixings for the purpose of indicating a correctly cured product. Nevertheless, in technical practice the coefficient may serve as a check on the cure of a known mixing; moreover, as the changes in the coefficient on ageing are of small magnitude, it is possible, from an analysis made some time after, to deduce the state of cure at the time of manufacture. In the case of a too rapid decay of a mixing of known composition, a knowledge of the coefficient of vulcanisation will indicate whether this was due to over-curing in the course of manufacture.

\* *J. S. C. I.*, 1922, 41, 228 T.

† *Bull. R. G. A.*, 1920, 2, 270.

## CHAPTER X

### FACTORS AFFECTING VULCANISATION

THE behaviour of a rubber during vulcanisation and the properties exhibited by the material after vulcanisation may be modified considerably by various factors incidental to either the method of preparation of the raw rubber or to the treatment which it undergoes at the hands of the manufacturer. As the result of work carried out almost entirely within the last decade, a great deal of information has accumulated from which it is possible to correlate the properties of the rubber with the conditions obtaining from the time the tree is tapped until the rubber is converted into an article of commerce.

#### PREPARATION OF RAW RUBBER

Raw plantation rubber as it comes on to the market may vary with respect to its outward appearance; for example, it may be in the form of smoked or unsmoked sheet, pale or dark crêpe, perhaps mould may be found on the surface, but these factors are not as a rule of great importance to the manufacturer. What are sometimes described as the "inner" properties are, however, of the utmost importance, and it is with respect to these that the manufacturer will require information, although it may be stated that actual purchase is not made on the basis of such properties. Of these inner properties the ones which should be as nearly constant as possible are the "tensile strength," the "rate of cure," and, to a lesser extent, the form of the stress-strain curve, which is frequently expressed by the "slope." In order to evaluate a sample of rubber some standard of comparison must be adopted, and it may be of interest to quote figures obtained by Schidrowitz and Goldsborough \* as a result of the examination of more than 500 samples taken from shipments from seven plantations. The following were the average figures obtained :

\* *I. R. W.*, 1917, 54, 187.

	Time of Cure (Hours).	"Type" (see p. 120).
Smoked sheet . . . . .	2.53	36.22
First latex crêpe . . . . .	3.04	35.53

The tests were carried out on a mixture of 100 parts rubber and 8 parts sulphur vulcanised at 141° C.

In an examination of some hundreds of samples from plantations in the Netherlands Indies, de Vries and Spoon \* obtained as average values :

	Tensile Strength. Kg. per sq. mm.		Rate of Cure. (Minutes).	
	Average.	Normal.	Average.	Normal.
Smoked Sheet { 1917 . . . . .	1.40	1.36-1.45	99	85-105
{ 1918 . . . . .	1.38	1.34-1.41	96	85-105
Crêpe { 1917 . . . . .	1.38	1.34-1.42	119	110-125
{ 1918 . . . . .	1.37	1.34-1.40	118	110-125

The test samples were obtained by vulcanising a mixture of 92½ parts rubber and 7½ parts sulphur at 148° C. to such a degree that a load of 1.30 kg. per sq. mm. produces an extension to 900 per cent. of the original length. The factors which affect the vulcanising properties will now be considered in detail.

*Age of Trees Tapped.*—In the case of trees which have reached the normal tapping age, say six years, de Vries † has shown that the rubber obtained possesses a tensile strength equal to that from older trees. On the other hand, the rubber from younger trees, say, 3 to 4½ years old, possesses comparatively low tensile strength, about 1.20 kg. per sq. mm., but the rate of cure is high, varying from 60 to 80 minutes (normal 110 minutes).

*Method of Tapping.*—According to de Vries, within certain limits alterations in the method of tapping, changes in the tapping system, tapping from higher or lower cuts, do not affect the rubber product, although heavier tapping than is normally practised yields a latex with a lower content of rubber, which after coagulation possesses a higher rate of cure.‡

*Anticoagulants.*—Of the reagents added to prevent premature coagulation

\* *Archief*, 1919, 3, 266.

† *Ibid.*, 1917, 1, 175.

‡ *Ibid.*, 1920, 4, 331.

of latex, formaldehyde is the only one which affects adversely the properties of the rubber, the time of cure being lengthened and the tensile strength decreased by addition of quantities in excess of 0.05 per cent. calculated on the latex.\* Sodium sulphite results in a slight decrease in the time of cure and a somewhat higher tensile strength. Sodium carbonate in the quantities usually employed is almost without effect on the vulcanising properties.

*Dilution of Latex.*—The effect of diluting latex with water is to increase the time of cure of the rubber produced; this is evident whether the rubber is made into sheet or crêpe.† Thus, to ensure uniformity, a standard dilution should be adhered to. In cases where brackish or tidal river water is employed for dilution of the latex the rubber may be affected by the retention of salts after coagulation. With increasing proportions of salts, such as chlorides, retained, there occurs corresponding increase in time of cure and a slight decrease in tensile strength. The effect is not so marked when the rubber is prepared as crêpe, owing to the partial removal of salts during the washing process.‡

In districts where the water supply is deficient, latex may occasionally be diluted with the serum remaining from a previous coagulation. In this way there is obtained a rubber having a shorter time of cure, which will be reduced according to the number of times the old serum is employed.§

*Coagulation.*—Although acetic acid is almost universally employed as coagulant, other reagents have been proposed from time to time.

Sulphuric acid gives a slow-curing rubber if used in slight excess over the amount necessary for complete coagulation; when not more than 0.1 per cent. is employed, the tensile strength does not appear to be markedly affected even after keeping the coagulated rubber for two and a half years.||

Hydrochloric acid gives a rubber having a slower rate of cure than that obtained with sulphuric acid. Moreover, the rubber has inferior qualities, becoming tacky in a comparatively short time.¶

Hydrofluoric acid, which has been marketed as a coagulant under the name of "Purub," tends to increase the time of cure of the rubber, but the tensile properties are equal to those of rubber coagulated with acetic acid.\*\*

The use of alum, which at one time was prevalent on small holdings in Malaya, has now been prohibited by the Government. The effect of alum in

\* *Bull. Imp. Inst.*, 1916, 14, 514; 1922, 4, 453; de Vries, and others, *Archief*, 1918, 2, 97.

† Eaton, *Bull. F. M. S.*, No. 27, 192; de Vries, *Archief*, 1917, 1, 25.

‡ Eaton, *Bull. F. M. S.*, No. 17, 1912, p. 23; Spoon, *Archief*, 1921, 3, 128.

§ *Bull. Imp. Inst.*, 1922, 4, 450; de Vries, *Archief*, 1921, 5, 294.

|| de Vries, *ibid.*, 1920, 4, 210; Eaton, *Bull. F. M. S.*, No. 27, p. 222.

¶ Eaton, *loc. cit.*; de Vries, *loc. cit.*

\*\* Eaton, *loc. cit.*; cf. also *Bull. Imp. Inst.*, 1922, 20, 455.

retarding the cure of the rubber is more marked than in the case where mineral acids are employed, especially when minimal proportions of each necessary for complete coagulation are taken.\* In the presence of sodium sulphite this retardation effect is eliminated.†

Formic acid gives results comparable with those obtained by the use of acetic acid, but a less proportion is necessary to bring about complete coagulation. An increase over the minimal amount, however, has a more marked effect in prolonging the time of cure than a similar excess of acetic acid.‡

According to de Vries (*loc. cit.*) irregularities in the results are met with, possibly due to inconsistency of composition of the acid supplied.

*Proportion of Acetic Acid Employed.*—Although variations in rubber, due to the influence of different coagulating agents, are only infrequently met with owing to the almost exclusive use of acetic acid, variations in the proportion of coagulant added may lead to the production of rubber possessing different vulcanising properties.

In normal factory practice sufficient acid is added to ensure complete coagulation, thus avoiding loss of rubber in the serum. If acid is added in excess of the minimal amount required, the rubber obtained exhibits a slower rate of cure with increasing proportions of acid used: § an increase of three to four times the normal proportions may, however, be employed without affecting seriously the time of cure or tensile properties.

By adding insufficient acid to ensure complete coagulation, a "first clot" may be obtained which yields a yellow to dark brown rubber, possessing a high rate of cure and low tensile strength. The second clot, formed by completing the coagulation, gives a pale rubber possessing normal vulcanising properties. The disparity between the two fractions is the less marked, the greater the proportions of the total rubber coagulated in the first clot.

*Treatment after Coagulation.*—Although, as is indicated in the foregoing paragraphs, the quality of the rubber may be influenced by several factors incidental to the operations of tapping, collecting and coagulating, the variations likely to arise from such causes are of small magnitude compared with those resulting from the treatment by which the coagulum is converted into a marketable form. Eaton and Grantham || have shown, for example, that there is present in the aqueous portion of latex some substance which tends to reduce the time of vulcanisation of the rubber. If in the course of preparation

\* Eaton, *loc. cit.*; de Vries, *loc. cit.*

† Stevens, *Bull. R. G. A.*, 1920, 2, 142.

‡ *Bull. Imp. Inst.*, 1922, 20, 454.

§ Eaton, *Bull. F. M. S.*, No. 27, p. 207; *Bull. Imp. Inst.*, 1922, 20, 454; Stevens, *Bull. R. G. A.* 1922, 4, 137; de Vries, Arens and Swart, *Archief*, 1917, 1, 40.

|| Eaton and Grantham, *J. S. C. I.*, 1915, 34, 989.

a proportion of the serum is allowed to remain in the rubber, the time of vulcanisation will tend to be less than that of rubber from the same coagulum which does not contain the serum substance to the same extent. In the preparation of sheet rubber the wet coagulum is rolled out and the resulting sheet with adherent serum is dried, and consequently the rubber prepared in this way will contain a proportion of the solids present in the serum. If, on the other hand, the coagulum is converted into crêpe, the washing process to which the rubber is submitted removes the adherent serum, and on this account crêpe rubber vulcanises more slowly than does sheet obtained from the same latex.

Although unsmoked sheet vulcanises more rapidly than crêpe, the same is not true of smoked sheet rubber, as the accelerating influence of the serum is masked by the effect of the smoking, which tends to retard vulcanisation; this is probably due to the action of phenolic substances present in the smoke, as Whitby \* has shown that rubber coagulated from latex containing phenols has a lower rate of cure than a control sample made from the same latex without such addition.

Quite apart from the accelerating substance already present in latex, a second accelerator may be formed as a result of putrefactive changes taking place after coagulation.† Thus, if the wet coagulum is not converted into sheet or crêpe immediately after formation, such changes will take place under ordinary tropical conditions and the vulcanising properties will be affected thereby.

For example, the time of cure of the rubber obtained by crêping a particular coagulum one day after coagulation was  $2\frac{3}{4}$  hours, whereas the crêpe prepared from the same coagulum after keeping for four days cured in  $1\frac{1}{2}$  hours; the time of cure of crêpe prepared after keeping the wet coagulum for ten days was  $1\frac{1}{4}$  hours.

The addition of antiseptics, such as formalin, was found to inhibit the change, as also did heating the coagulum; keeping the wet coagulum after such treatment did not result in the formation of accelerating substance.

The action was also inhibited by keeping at a temperature of 0° C., but on removing the wet coagulum from cold storage and keeping at tropical temperature the putrefactive change was found to proceed normally, and a rapidly curing rubber was obtained.

As will be inferred from these observations, rubber, which after coagulation is not immediately converted into sheet or crêpe, but is allowed to remain in the form of a slab for some time, will possess a high rate of cure as compared

\* J. S. C. I., 1916, 35, 497.

† Eaton and Grantham, *ibid.*, 1916, 35, 715.



with rubber which has not been so treated. Rubber prepared by this process of "maturation," as it is called, will give a satisfactory product after 1 to 1½ hours vulcanisation at 140° C. in a mixing containing 90 parts of rubber and 10 parts of sulphur; under similar conditions normally prepared sheet or crêpe rubber will require from 2½ to 3 hours. This high rate of cure is acquired in the first six days of maturation, and if at the end of this period the slab is made up into crêpe the characteristics of rapid vulcanisation still persist. It is obvious that rubber which may appear on the market in the form of slab will possess this high rate of cure unless special precautions have been adopted, such as by the addition of antiseptic, to prevent putrefactive change.

This maturing process may take place, although to a limited extent, in the preparation of sheet rubber, especially unsmoked sheet, which is dried slowly at ordinary temperature. Sheet rubber when first rolled out and hung up to dry is virtually a thin slab, and if, for any reason, drying does not take place as quickly as usual, the putrefactive changes may occur in the early stages of the drying operation.

During the maturing of slab rubber, part of the nitrogenous constituent normally present undergoes decomposition, yielding substances which are more volatile and more readily soluble in water than the parent substance. Thus slab rubber usually contains a lower proportion of nitrogen than the other grades, and a lower proportion still is found in crêpe which has been prepared from slab rubber. The loss of nitrogenous matter is, however, reduced if the slab is first smoked.

The foregoing remarks show to what an extent the properties of the rubber may be influenced by changes taking place in the coagulum if it is not converted into sheet or crêpe within a short time after its formation. It has also been shown that the properties may differ according to whether the rubber is made into sheet or crêpe, owing to the presence or otherwise of serum substances. Other factors involved in the production of these grades may now be considered.

It has been explained that in the preparation of crêpe the almost universal practice is to add sodium bisulphite to the latex before coagulation in order to ensure the production of a pale-coloured rubber. The use of sodium bisulphite in the proportions normally employed does not appear to affect the properties of the rubber to an appreciable extent, Eaton \* having noted only a slight increase in the time of vulcanisation; according to de Vries † the time of cure is lowered and the tensile strength improved slightly.

\* *Bull. F. M. S.*, No. 27, p. 210.

† *Archief*, 1918, 2, 97.

The effect of excessive mechanical working in the preparation of crêpe rubber has been investigated,\* and it has been found that passing the rubber between the washing rolls as many as seventy times has no appreciable effect, either on the time of cure or on the tensile strength. Eaton,† however, states that in the first stages of the preparation of crêpe there is a small but nevertheless positive retardation of cure and decrease in tensile strength, but when the crêpe has once been brought to the thin form, further passage between the rolls does not produce any effect.

It will be understood that in the preparation of crêpe the rubber is not allowed to become heated, as it is subjected to a continuous stream of water. Passage through the crêping machine must, therefore, not be confused with ordinary mastication or milling.

The manner in which the rubber is dried is not without effect on the rate of cure. It has been previously stated that in the drying of sheet the development of substances which hasten the cure of the rubber will depend on whether the rubber is dried slowly or not.

The temperature at which drying takes place may also affect the rate of cure; sheet dried at 120° to 130° F. will vulcanise more quickly than sheet dried at normal tropical temperature, i. e. 85° F.‡ The effect of heat is thus to cause an increase in the rate of cure, possibly owing to acceleration of the putrefactive changes in the early stages of drying; if the heating takes place in a smoke-laden atmosphere there will be two opposing factors involved, the effect of the heat tending to reduce, and the effect of the smoke constituents tending to increase, the time of cure.§

*Special Methods of Coagulation.*—So far, the variations which may occur in rubber coagulated by means of acetic acid have been discussed. It may be of interest to consider how the properties of the rubber are affected by adopting special methods of coagulation. Of these the two most important processes are those depending on evaporation of the latex and those in which coagulation is allowed to take place spontaneously.

From the experiments of Eaton and Grantham it was clear that the drying of serum on the rubber, even though putrefactive changes did not occur, resulted in a quick-curing rubber, and it is not surprising to find that by evaporating latex completely the residual rubber also possesses a high rate of cure.||

\* *Bull. Imp. Inst.*, 1916, 4, 533; 1922, 14, 436; de Vries and Swart, *Archief*, 1917, 1, No. 1.

† *Bull. F. M. S.*, No. 27, p. 197.

‡ Eaton, *ibid.*, No. 27, p. 182.

§ Eaton, *J. S. C. I.*, 1917, 36, 1226.

|| *Bull. F. M. S.*, No. 27, p. 78; Stevens, *J. S. C. I.*, 1922, 41, 326 T.

Rubber which has been prepared by any of the processes involving evaporation of the latex, such as by delivering on to a hot drum or by spraying into a heated chamber, will therefore vulcanise rapidly. It is interesting to note that evaporated latex rubber which has been extracted with water or with acetone still possesses this property.\*

The tensile properties of evaporated or sprayed latex are generally found to be equal to or higher than the average for sheet rubber, although Stevens † has published figures indicating that this is not always the case.

Spontaneous coagulation may take place in presence or in absence of air, and in each case the rubber produced possesses good tensile properties and a comparatively high rate of cure.‡ In cases where coagulation takes place in presence of air, putrefactive changes occur, and consequently the rubber possesses a higher rate of cure than when the coagulation proceeds under anaërobic conditions.

*Changes occurring after Rubber is Prepared.*—Under ordinary conditions the higher grades of rubber may be stored for many years without undergoing apparent alteration; slight darkening may occur in pale crêpe and smoked sheet may appear dull on the surface. That the tensile properties are not adversely affected on storage has been demonstrated by Stevens,§ who has found the tensile strength after vulcanisation to be normal even after storage for thirteen years. Similarly, de Vries || has recorded experiments with rubber stored for two to four years in a cupboard or in chests. In the case of first quality rubber the tensile strength was practically the same as originally, and some of the lower grades gave comparable results. Grades such as bark and earth scrap, however, showed a distinct deterioration. It is interesting to note that both Stevens and de Vries found a tendency towards a greater uniformity in rate of cure, fast-vulcanising rubbers generally exhibiting a decrease and slow-curing rubbers a slight increase in rate, after storage.

There are, however, certain surface defects which are liable to develop in sheet rubber, particularly unsmoked sheet, after storage or even during transit. Of these, one is the growth of moulds, the other is the phenomenon known as "rustiness."

Light mould growths are frequently met with in unsmoked sheet, and their development is aided by the presence in the sheet of serum substances which provide food material, generally absent in crêpe rubber. Smoking

\* Stevens, *loc. cit.*

† *I. R. J.*, 1923, 65, 274.

‡ Eaton and Grantham, *Bull. F. M. S.*, No. 27, p. 286; *Bull. Imp. Inst.*, 1922, 20, 439; Spoon, *Archief*, 1919, 3, 335; 1920, 4, 289; de Vries and Spoon, *ibid.*, 1920, 4, 308.

§ *J. S. C. I.*, 1918, 37, 340 T.; *Bull. R. G. A.*, 1921, 3, 289.

|| *Archief*, 1921, 5, 140.

sheet rubber generally prevents the development of mould, but, according to Stevens,\* the smoke constituents absorbed by the rubber are not sufficiently fungicidal to ensure this in all cases. Treatment with formalin is not effective, but sodium silicofluoride, if added to the latex before coagulation in the proportion of 0.6 gr. per litre, gives satisfactory results. Even when this reagent is used, it is important that the sheets are not packed in a wet condition, otherwise moulds may develop.† Rubber obtained from latex previously treated with sodium silicofluoride exhibits a somewhat lower rate of cure than the normal, and possesses slightly improved tensile properties. Although light moulds may develop on the surface there is little evidence to show that the properties of the rubber are affected thereby; Stevens states that with heavier growths variations may result, the grey-green mould which develops in daylight having a retarding influence on the rate of cure, while the black and yellow pin-head type which develops in the dark had a slight accelerating effect.

“ Rustiness ” is the name given to the appearance sometimes produced in smoked sheet rubber, which when stretched and allowed to retract appears opaque at the part where stretching has taken place, owing to the surface being covered with a fine brown powder.

According to Eaton ‡ this phenomenon is due to the presence of a film of dried serum which is transparent but is comparatively brittle, so that when the surface of the rubber is stretched the film is broken. Hellendoorn § states that the film is not actually dried serum, but a decomposition product formed by an anaërobic micro-organism. Whatever the nature of the film, the substance present appears to be without effect on the properties of the rubber, neither the rate of cure nor the tensile strength being abnormal.

\* *Bull. R. G. A.*, 1921, 3, 190, 243, 472.

† *Bull. F. M. S.*, No. 27, 300.

† Stevens, *ibid.*, 1922, 4, 331.

§ *Archief*, 1919, 3, 430.

## CHAPTER XI

### COMPOUNDING INGREDIENTS

ALTHOUGH during the process of vulcanisation rubber acquires improved tensile properties which render it of greater utility than the original raw material, the uses to which vulcanised rubber could be adapted would be very much restricted were it not for the fact that by the addition of suitable compounding ingredients the properties may be subjected to considerable modification. A "pure" vulcanised rubber—in other words, a rubber containing no adjuvant other than the sulphur necessary for vulcanisation—would find only limited industrial application. Thus, in addition to rubber and sulphur, technical mixings almost invariably contain ingredients added for the purpose of imparting specific properties to the product, and in some instances others added to facilitate the process of manufacture. In general, the materials introduced may be divided into (a) pigments or colouring matters; (b) softening agents added to render the rubber more easily manipulated during the operations of calendering, extruding, etc.; (c) diluents or substances added to produce a cheaper material; (d) fillers which improve the mechanical properties; (e) accelerators, or substances which hasten the vulcanisation process. This classification is not to be regarded as rigid, since, for example, some pigments act also as fillers which improve the mechanical properties and as accelerators of vulcanisation. Again, many substances which may be classed as diluents are often added for the express purpose of softening the masticated rubber.

#### PIGMENTS

The choice of pigments must be governed by a consideration of the conditions obtaining during vulcanisation, which will in turn depend upon the method of vulcanisation to be adopted. If ordinary hot vulcanisation is to be employed, the colour chosen must be capable of withstanding a temperature of, say, 150° C. for three hours; this alone is sufficient to exclude a considerable number of organic dyestuffs. The fact that the heating takes place in the presence of sulphur is another factor which must be considered. Under such circumstances white lead reacts with sulphur to form black lead sulphide, so that white lead cannot be used to give a white vulcanised rubber. Similarly,

it is not possible to use litharge as a yellow colouring material, although it is largely employed, in the manufacture of black goods, as an accelerator.

As a general rule, only those pigments with a good colouring power are suitable for use in rubber mixings, since the rubber itself after vulcanisation is of a dark colour, and the effect of pigments is consequently somewhat obscured.

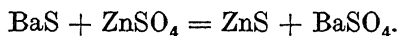
If the sulphur chloride process of vulcanisation is to be adopted, the pigment must withstand the action of the vulcanising agent itself, of hydrochloric acid, which may be produced by interaction with moisture, and of ammonia with which any acidity is subsequently neutralised.

Where a cold sulphur process, such as the Peachey gas process, or one based on the use of an active accelerator, is to be employed, the range of permissible pigments and colours is almost unrestricted.

*White Pigments.*—Zinc oxide is unquestionably the most widely used white pigment, and owes its popularity not only to its excellent colouring power, but also to the toughness which it imparts to the vulcanised rubber.

In the manufacture of zinc oxide on a large scale the "direct" American process or the "indirect" French process may be employed. In the one case the ore is reduced to give metallic zinc, which is oxidised directly to zinc oxide; in the other case the ore is treated to produce zinc which after purification is burnt to form the oxide. According to Green \* the particles of the oxide as made by the American process are from 0.4 to 0.6 $\mu$  in diameter, whereas in that made by the French process the particles are somewhat smaller, being from 0.3 to 0.4 $\mu$ ; a microscopical examination may thus serve to distinguish between samples of the pigment of different origin. Either process yields a product containing hexagonal prisms, marked by the occurrence of twins, triplets or quadruplets. Cadmium sometimes occurs as an impurity, in which case the material possesses a marked yellowish tint which may deepen somewhat after vulcanisation. On the other hand, if lead is present, the original material may possess a satisfactory white colour, but during vulcanisation considerable darkening takes place.

*Lithopone, Ponolith, or Orr's Zinc White*, as it is variously described, consists essentially of a mixture of barium sulphate and zinc sulphide in approximately molecular proportions. The principle of the method of preparation is based on the interaction of zinc sulphate with barium sulphide to form barium sulphate and zinc sulphide, both of which are precipitated from the mixed solutions:



A pigment prepared in this manner and containing molecular equivalents of the reaction products would consist of 70.5 per cent. barium sulphate and

\* *Chem. and Metall. Eng.*, 1923, 28, 53.

29.5 per cent. zinc sulphide. In practice, part of the barium sulphide is precipitated with zinc chloride, the remainder then being added together with zinc sulphate, the final composition being approximately the same. The precipitate thus obtained possesses only moderate colouring power, but after calcination and cooling suddenly by plunging into water the pigmentary value is much improved. While the pigment is being calcined a proportion of the zinc sulphide may undergo conversion into zinc oxide, so that this will be found as a constituent of commercial samples. Lithopone possesses a fine white colour of greater intensity than a simple mixture of barium sulphate and zinc sulphide in the same proportions. The colour tends to darken on exposure to light, this being due, it is stated, to the presence of traces of zinc chloride.\* According to Green (*loc. cit.*) the diameter of the particles in lithopone is 0.3 to 0.4 $\mu$ . Zinc sulphide is sometimes used alone as a white pigment, but not to any considerable extent.

*Titanium Oxide or Titanium White*,  $Ti_2O_3$ , is a very finely divided pigment of exceedingly high colouring power; in fact, superior to zinc oxide in this respect. The comparatively high price is probably the only reason why it is not more extensively employed at the present time.

*Antimony Oxide*,  $Sb_2O_3$ , known as "Timonox," possesses fairly good pigmentary properties, but exhibits a tendency to alter in shade during vulcanisation owing to the formation of antimony trisulphide.

*Whiting* and other forms of calcium carbonate, such as precipitated chalk, are employed to a considerable extent, and, besides possessing pigmentary value, are not without interest as mild "reinforcing" fillers.

Other white fillers of less importance as pigments, but of interest from other points of view, are barytes, clays of different types, asbestos powder, mica, and French chalk or talc.

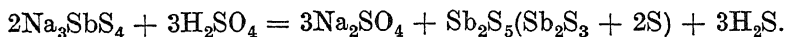
*Antimony Sulphide, Golden Sulphide or Antimony Sulphuret* is probably the most extensively used red or orange pigment. The general method of preparation consists in dissolving native antimony sulphide (stibnite) together with sulphur in an alkaline sulphide to form a thioantimonate, from which the sulphide is obtained, on addition of acid, as a precipitate varying in colour from orange-red to a golden yellow. The sulphide may consist entirely of the trisulphide, or in addition a higher sulphide such as the pentasulphide may be present according to the conditions of the precipitation. The formation of pentasulphide may be represented as follows:



Sodium Thio-antimonate

\* Steinau, *C. T. J.*, 1921, 69, 271.

The sodium thio-antimonate, which in the commercially pure form,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ , is known as Schlippe's salt, is decomposed by acids with formation of antimony pentasulphide and liberation of hydrogen sulphide



The precipitation of the pentasulphide quantitatively is accomplished only under certain experimental conditions, and as a rule a considerable proportion of the trisulphide is formed together with free sulphur. Frequently the stibnite is dissolved in calcium sulphide, in which case on decomposing the thio-antimonate with sulphuric acid, calcium sulphate is precipitated together with the antimony sulphide. Thus "golden sulphide," as it appears on the market, may contain antimony pentasulphide, antimony trisulphide, sulphur, and calcium sulphate in varying proportions.

The free sulphur as determined by extraction with carbon disulphide is usually declared so that purchasers may know how much sulphur, which will, of course, contribute towards the vulcanisation effect, is being added as a constituent of the pigment. There is also a possibility of the antimony pentasulphide undergoing decomposition during the heating period with formation of the trisulphide and liberation of free sulphur, which will also be available for vulcanisation.

The existence of antimony pentasulphide in commercial samples of golden sulphide has been disputed,\* although the presence of sulphur in combination with antimony in proportions higher than that represented by the formula  $\text{Sb}_2\text{S}_3$  is admitted. Whether the higher sulphide present is the pentasulphide or a "tetrasulphide,"  $\text{Sb}_2\text{S}_4$  (*i. e.* antimony thio-antimonate  $\text{Sb}'''\text{SbS}_4$ ), is of relatively less importance than the question whether this higher sulphide is liable to undergo decomposition on heating at vulcanising temperatures with liberation of sulphur available for vulcanisation.

It has been shown by Luff and Porritt † that certain samples of golden sulphide actually yield additional sulphur when heated at  $150^\circ\text{C}$ ., and the possibility of samples containing a sulphide capable of yielding sulphur at vulcanising temperatures must be considered.

It is not clear why the presence of pentasulphide in golden sulphide of antimony is regarded as essential or even desirable, since the pigmentary value of samples containing pentasulphide is not superior to that of the trisulphide. The presence of a higher sulphide introduces a degree of uncertainty regarding the sulphur available for vulcanisation, whereas in the case of the trisulphide

\* *E. g.* Kirchhof, *Z. Anorg. Chem.*, 1920, **112**, 67; Short and Sharpe, *J. S. C. I.*, 1922, **41**, 109 T.

† *Ibid.*, 1921, **40**, 275 T.



this would be ascertained by determining the sulphur extractable at ordinary temperatures with carbon disulphide.

Golden antimony sulphide is converted into the black modification on heating to about 200° C., but the change takes place gradually at somewhat lower temperatures, and may even be brought about at 100° C. by repeatedly evaporating a sample with water. In most cases the colour is preserved during vulcanisation, although samples containing traces of impurities such as hydrochloric acid will darken under these circumstances.

Besides functioning as a pigment, antimony sulphide may act as an accelerator,\* but whether this behaviour is restricted to samples containing sulphide higher than the trisulphide is not certain.

*Crimson Antimony* or *Antimony Vermilion* is less frequently employed in this country, but is sometimes used in France. The method of preparation consists in adding to a solution of antimony trichloride or tartar emetic, sodium thiosulphate, whereupon a precipitate is obtained which becomes scarlet on heating the liquid. The composition of antimony vermilion approximates closely to that of antimony trisulphide, but the oxide is frequently present and sometimes the oxychloride.

*Vermilion, Mercuric Sulphide*,  $\text{HgS}$ , is also employed as a rubber pigment, particularly in the manufacture of hard rubber or vulcanite for which antimony sulphide is unsuitable. Owing to the longer period of vulcanisation and the higher temperatures employed in the manufacture of ebonite, antimony sulphide does not retain its colour as it does when used in soft rubber goods, but gradually darkens.

*Iron Oxide* or "*Red Oxide*,"  $\text{Fe}_2\text{O}_3$ , is largely used as a red pigment, and, as will be seen later, is of interest on account of its reinforcing action in vulcanised rubber. It may be noted that iron oxide does not blacken during vulcanisation. Natural earths, or ochres, which owe their colour to iron oxide, are also employed to a limited extent.

A number of organic lake pigments, for example, certain alizarine lakes, satisfactorily withstand vulcanising conditions and are frequently employed in hot vulcanisation. Many of the oil soluble colours, such as oil red S (toluene-azo-toluene-azo- $\beta$ -naphthol), which are more suitable for transparent sheet, may be successfully adapted to the colouring of rubber goods.

*Yellow pigments* are not used to any considerable extent, but there are a number which give satisfactory results, notably the sulphides of arsenic and cadmium; zinc chromate is also capable of application for hot or cold vulcanisa-

\* Anderson and Ames, *J. S. C. I.*, 1923, 42, 136T.

tion, but lead chromate cannot be used for hot vulcanisation owing to blackening occurring.

The most extensively used *green pigment* is Chromium Oxide,  $\text{Cr}_2\text{O}_3$ , which is resistant to the conditions of both hot and cold vulcanisation.

The *blue pigments* in common use are Ultramarine and Prussian Blue. While ultramarine gives satisfactory results in hot vulcanisation, it cannot be employed when the sulphur chloride process is to be adopted, owing to the colour being discharged by the hydrochloric acid formed. Prussian Blue, on the other hand, does not retain its colour during hot vulcanisation, but is not affected by sulphur chloride.

*Black pigments* are represented by the various forms of carbon, of which lamp black, vegetable black and gas black are the most outstanding. Lamp black is made by burning oils, fats and other organic matter in an air supply insufficient for complete combustion. The soot thus formed is deposited in a series of chambers in different degrees of fineness, the heaviest collecting in the first chambers and being sold as lamp black, the lighter or finer portions collecting in the end members of the series and being placed on the market under the name of vegetable black.

"Gas black," or "carbon black," as it is usually described, is manufactured largely in America by the incomplete combustion of natural gas which issues from the earth in certain localities. The flame is allowed to impinge on a moving metal surface from which the deposited carbon is removed by means of scrapers. The particles of carbon black have been described as having a diameter of  $0.15\mu$  as compared with  $0.3$  to  $0.4\mu$  for the particles of lamp black,\* but in all probability the average diameter is even smaller than this, the dimensions being such as to be beyond the resolving power of the microscope.

According to analyses given by Neal and Perrott,† carbon black as marketed contains fixed carbon in proportions varying from 79 to 92 per cent., moisture from 2 to 7 per cent., and volatile matter to the extent of 5 to 13 per cent. Absorbed gases are present and may be removed by means of a Töpler pump. The gas pumped off at ordinary temperatures has a composition almost identical with that of air, whereas that removed at higher temperatures, *e.g.*  $445^\circ\text{C}$ ., contains a high proportion of carbon monoxide and carbon dioxide. The actual specific gravity of carbon black which has been freed from moisture varies from 1.7 to 1.88 according to the composition of the sample.

"Black hypo," which is an impure form of lead thiosulphate, was at one time

\* Green, *Chem. and Met. Eng.*, 1923, 28, 53.

† "Carbon Black: its Manufacture, Properties and Uses," *U.S. Bureau of Mines Bulletin*, 192, 1922.

employed as a black pigment. The method of preparation generally adopted is to heat lead carbonate with sulphur, whereby lead thiosulphate, sulphate and sulphide are produced, the latter giving the material the characteristic black colour. "Black hypo," therefore, consists of a mixture of these compounds together with free sulphur, which may be present in quantity sufficient to obviate the necessity of adding sulphur as such to bring about vulcanisation.

### SOFTENING AGENTS

In order to aid in the subsequent working of a rubber mixing, it is sometimes necessary to add certain materials which render the rubber plastic. The substances added are chiefly of an organic nature and comprise reclaimed rubbers, rubber substitutes or "factices," "mineral rubber," paraffin hydrocarbons and, to a lesser extent, vegetable oils.

### RECLAIMED RUBBER

Reclaimed or regenerated rubber is the name given to the material recovered from waste or used rubber goods. It is sometimes spoken of as "devulcanised" rubber, but this is a misnomer, since most of the characteristics of vulcanised rubber still persist in the products obtained by the methods commonly employed.

All efforts to remove the combined sulphur in vulcanised rubber and so to regenerate the rubber in its original form have so far been unsuccessful. All that has been accomplished is to render the rubber sufficiently plastic to allow of its being manipulated in the same manner as can the raw material. Ordinary vulcanised rubber without previous treatment cannot be rendered plastic, as it merely falls into a coarse powder or "crumb" on passing between the mixing rolls.

The waste rubber which is available may consist of vulcanised rubber, with which is incorporated the usual filling materials, and in addition there may be present fabric, metal, and other extraneous matter. The simplest case is that in which the waste rubber is not associated with fabric or other undesirable material. By grinding to a fine crumb and submitting to a high pressure and elevated temperature a homogeneous mass may be obtained from which articles may be moulded directly. Or the crumb may be heated with paraffin hydrocarbons to give a soft material which may be masticated in the ordinary way. A large number of plasticising agents have been patented, for example, turpentine, aniline, creosote, phenols and other high boiling organic liquids, but these are of comparatively little practical interest. Such a product is usually spoken of as "reformed" as distinct from "reclaimed" rubber, to obtain which the crude waste has to be submitted to a chemical treatment.

This is necessary in cases where the waste consists of tyres, shoes, etc., in which the rubber is intimately commingled with cotton fabric. The rubber is isolated from the mixture by means of either the "acid" or the "alkali" process.

In the acid process the crude material is ground to a crumb and freed from dirt by sieving, metal being removed by means of a magnetic separator, after which it is heated with dilute sulphuric acid at ordinary atmospheric pressure. In this way the fabric present is destroyed and at the same time some of the inorganic constituents of the vulcanised rubber may be dissolved out. The excess of acid is removed by washing with water, and the crumb is then exposed to an atmosphere of steam at a high pressure and temperature which renders the rubber plastic so that it can be worked on a mill in the ordinary way.

In the "alkali" process the ground scrap is treated with dilute caustic soda solution in an autoclave at a temperature of about 170 to 180° C., which is effective in dissolving the cellulose and a considerable proportion of the "free" sulphur in the vulcanised rubber. At the high temperature employed the rubber becomes plastic, so that after washing free from alkali and drying the crumb may be rolled out into sheets on the mill.

### RUBBER SUBSTITUTES

Rubber substitute, or "Factice," is the description applied to certain materials which bear some resemblance to rubber and which are prepared by "vulcanising" vegetable oils. Two varieties, the white and the brown substitute, are manufactured.

White Substitute is obtained by the action of sulphur chloride on vegetable oils, such as cottonseed oil, and when first prepared forms an amber-coloured, jelly-like mass which after grinding appears almost white.

Brown Substitute is obtained by heating the vegetable oil with sulphur, the reaction yielding a mass which is dark brown in colour but otherwise resembles the white substitute.

These substitutes are insoluble in most organic solvents, but are readily saponifiable on heating with aqueous or alcoholic alkali.

### MINERAL RUBBERS

Mineral rubber, "M.R.," "Gilsonite" or "hydrocarbon" are the names under which certain natural or artificial bituminous substances are known. The name mineral rubber was originally given to the naturally occurring elaterite found in Derbyshire, as it was then thought to be a form of caoutchouc. The name is now often used to include the asphaltic residues obtained in the

distillation of petroleum as well as the naturally occurring forms of which gilsonite is one.

### OTHER SOFTENING AGENTS

Among other organic softening agents are paraffin wax, high-boiling petroleum, cottonseed oil, and aniline, which is also an accelerator. Glue, which is now largely employed, especially in America, as a reinforcing filler, has also been suggested for use as a means of incorporating finely divided mineral fillers in order to avoid agglomeration or caking of the particles on the mill.

### REINFORCING FILLERS

For some considerable time past it has been customary to incorporate in mixings certain substances which increase the toughness or the wearing properties of the vulcanised rubber. The materials employed have been adopted as a result of practical experience, and not from the results of systematic investigation; later work has, however, served to emphasise the wisdom of the choice in the majority of cases.

One of the earliest investigations into the effects produced by filling materials and pigments was that of Heinzerling and Paal,\* who determined the tensile and chemical properties of a variety of mixings containing such substances as zinc oxide, French chalk, fluorspar, antimony sulphide, litharge and magnesia. The proportions were, however, chosen with an entire lack of system, and it is difficult to draw deductions from their results.

A more systematic series of experiments was later carried out by Ditmar,† who adopted the principle of adding to a mixture of rubber and sulphur increasing proportions of each particular compounding ingredient and noting the tensile properties of the vulcanised material.

In the case of light magnesium carbonate, for example, increasing proportions up to 25 per cent. by weight were found to enhance the tensile strength considerably.

The addition of zinc oxide in small quantities, such as 1 per cent., was found to increase the extensibility, but with higher proportions a reduction took place; the tensile strength was found to be improved.

Addition of barytes in proportions up to 25 per cent. was practically without effect, both the breaking load and elongation being unaltered. On the other hand, powdered glass caused an increase in tensile strength but did not affect the extensibility.

A comparison of the effects of increasing proportions of zinc oxide and talc

\* *J. S. C. I.*, 1892, 11, 536; 1893, 12, 51; cf. Weber, *The Chemistry of India Rubber*, p. 162.

† *Gummi Zeit.*, 1906, 20, 733, 844, 1077; 1906, 21, 103, 234, 418.

on a mixing of 100 parts rubber and 5 parts sulphur was made by Beadle and Stevens.\* To this basic mixing the mineral ingredients were added in proportions of  $\frac{1}{2}$ , 2, 5, 15, 40 and 75 parts by weight respectively, and each sample cured for three hours at 135° C.

It was found that zinc oxide produced a greater toughening effect than an equal weight of talc, but, in contradistinction to what had been observed by Dittmar, it was found that even small proportions of zinc oxide, as, for example,  $\frac{1}{2}$  per cent., produced a marked resistance to stretching. Beadle and Stevens, however, were working with a mixing containing a lower proportion of sulphur, and the extension was recorded only at small loads. The addition of small proportions of talc was found to increase the extension with a given load, or, in other words, to produce a softening effect on the vulcanisate. This was the case up to 2 per cent., but beyond this point the mixing became tougher and the extension with a given load decreased regularly as the proportion of talc increased. Zinc oxide in proportions up to 10 per cent. caused a decrease in the sub-permanent set, after which increase in the amount of pigment brought about an increase in the set; talc, on the other hand, caused an increase in the sub-permanent set even when added in small proportions. Hysteresis curves were drawn by means of the Schwarz machine † over five successive cycles of extension and retraction at a load of 0.2 kg. per sq. mm. The area enclosed by the loops corresponding to energy absorbed was small in the case of the mixing containing 40 parts of zinc oxide, but was greater in the sample containing talc, and even more pronounced in the case of the basic mixing.

With the exception of the researches quoted, little exact knowledge regarding the specific effect of compounding materials was available until 1920, when Wiegand,‡ in a most stimulating publication, brought out very clearly the manner in which the tensile properties of a vulcanised rubber were influenced by a specific attribute of the filling material with which it had been incorporated, namely, the average particle size. For a long time it had been recognised that pigments possessed a higher colouring power per unit weight when in a fine state of division, and on this account alone finely divided materials were chosen in preference to coarser ones; certainly particles of macroscopic dimensions were excluded owing to the uneven appearance which would result from their introduction. Further, the presence of comparatively large particles would be undesirable in goods like the inner tubes of cycles owing to the possibility of air leaks taking place through displacement of the particles. In a general way, then, the manufacturer had come to regard fineness of division as an

\* *J. S. C. I.*, 1911, 30, 1421.

† *I. R. W.*, 1911, 44, 442.

‡ *I. R. J.*, 1920, 60, 379, 423.

essential in filling materials. Nevertheless it was not until recently that the fineness of division of pigments and fillers used in the industry came to be recognised as a contributory factor in determining the tensile properties of the vulcanised rubber. That the importance of particle size was ultimately realised is instanced by the statement of Twiss,\* to the effect that, "generally speaking, the finer the state of aggregation of a mineral substance the greater the strength and toughness of the rubber mixing into which it is introduced."

The introduction of clay prepared by a process of deflocculation † as a suitable ingredient for rubber mixings again served to indicate the trend of ideas.

The results obtained by Wiegand, however, showed in a very striking manner how the tensile properties of vulcanised rubber could be correlated with the particle size of the filling agent.

The experimental method consisted in adding to a basic mixing of Fine Para rubber, litharge and sulphur increasing proportions by volume of various pigments or filling materials. The original mixing chosen was as follows:

	By Weight.	By Volume.
Rubber . . . . .	100	100
Litharge . . . . .	30	3
Sulphur . . . . .	5	2½

This particular mixing was adopted on account of the fact that over a range of cures varying from fifteen minutes to forty-five minutes at 141° C. practically equivalent tensile properties would result, and in this way variations in the time of cure due to the introduction of the filling materials would be eliminated. The addition of the various ingredients on a volume basis was an advance in experimental technique, as the effect of each constituent could be compared directly volume for volume. This would not be possible if the pigments were introduced in varying proportions by weight owing to the differences in specific gravity of the materials examined. After introduction of the required volume of pigment the mixing was vulcanised at the temperature stated for a standard time and straight test-pieces extended on a Scott machine and the stress-strain curve obtained. It may be stated that the load was calculated to total cross-sectional area of the sample under test, and not to the area of actual rubber presented. The curves obtained with increasing volumes of a particular filler

\* *Ann. Rept. Appl. Chem.*, 1919, 4, 324.

† Schidrowits, Feldenheimer and Plowman, E.P., 106, 890, 1919.

were plotted on the same graph, and it was thus possible to ascertain at a glance the effect of progressive addition of each of the filling agents examined.

The difference in behaviour exhibited among the various adjuvants was judged from the point of view of the tensile strength and the displacement of the stress-strain curve, at each proportion added. The filler affecting the position of the stress-strain curve to the least extent was barytes, successive additions of which up to 150 volumes per 100 volumes of rubber resulting merely in a corresponding reduction in tensile strength. Barytes is therefore regarded solely as a diluent, since its addition does not in any way improve the tensile properties. Carbon black, or gas black, was found to yield the most satisfactory results, progressive addition causing the curve gradually to approach the load axis; at the same time the tensile strength increased up to addition of 30 volumes, and at 40 volumes was equal to that of the original, after which it fell away suddenly. After the addition of 15 volumes the stress-strain curve had lost the characteristic form exhibited by a "pure" rubber mixing and was almost linear, *i. e.* in accordance with Hooke's Law. Carbon black is, therefore, a "reinforcing" pigment, that is to say, it improves the tensile properties in that the resistance to stretching is increased and the tensile strength enhanced by its addition to a rubber mixing. Similar properties were exhibited by other fillers, such as zinc oxide, but in this case the decrease in tensile strength began at 20 volumes and the displacement of the curve was not so marked as with carbon black.

It should be mentioned that all the fillers were assumed to be inert, that is to say, not to undergo chemical change or act as "accelerators" of vulcanisation, and therefore any difference in behaviour will be due solely to a difference in particle size.

In the case of carbon black, zinc oxide and china clay, the effect of progressive additions on the position of the stress-strain curve is comparable with that of progressive times of vulcanisation in a rubber-sulphur mixing; barytes, however, does not act in this way.

In order to express the results numerically, Wiegand took as one criterion the area enclosed between the whole stress-strain curve and the elongation axis (Fig. 6), which is a measure of the energy of resilience, or the energy stored in the rubber when extended to its breaking-point; these areas were measured with a planimeter and the results calculated to foot-pounds per cubic inch of original stock.

The displacement of the stress-strain curve was also determined by a comparison of the load necessary to produce a given elongation, in which case



the higher this value the tougher or more resistant to stretching is the vulcanisate.

The average particle size of each of the fillers was determined by direct microscopical measurement, and the specific surface, that is to say, the surface exposed per unit volume, calculated and expressed in square inches per cubic

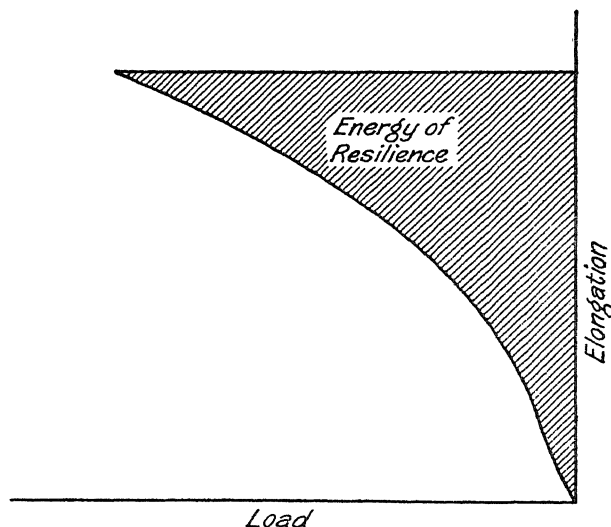


FIG. 6.

inch of pigment. The following results were obtained with the mixing containing 20 volumes of each of the filling agents specified :

Filler.	Apparent Surface.	Displacement of Stress-strain Curve.	Total Energy of Resilience.
Carbon black . . . . .	1,905,000	42	640
Lamp black . . . . .	1,524,000	41	480
China clay . . . . .	304,800	38	405
Red oxide (Ferric Oxide) . . . . .	152,400	29	355
Zinc oxide . . . . .	152,400	25	530
Glue . . . . .	152,400	23	344
Lithopone . . . . .	101,600	—	—
Whiting . . . . .	60,950	17	410
Fossil flour . . . . .	50,800	14	365
Barytes . . . . .	30,480	8	360
			Base
			450

The figures generally indicate that the smaller the particle size, and hence the greater the specific surface, the higher are the tensile properties imparted to the vulcanised rubber as indicated by the displacement of the stress-strain curve. The positions of zinc oxide and whiting in the column showing energy of resilience are, however, anomalous when compared with the order of particle size.

Wiegand attributes the enhanced value of finely divided substances to the higher dispersion affording a greater surface contact between the filler and the rubber; thus the system offers greater resistance to forces tending to separate the two phases at the interface.

The tensile properties are, therefore, of a high order only when the individual particles of filler are surrounded or "wetted" by the rubber; the sudden falling away of the tensile strength when a certain volume of filler has been introduced is regarded as due to the volume present being too great to admit of complete wetting, with the result that aggregates of the filler are formed, with a consequent weakening of the system.

A somewhat similar series of experiments was carried out by North,\* who added increasing volumes of various fillers to a pure rubber-sulphur mixing. The complication introduced by Wiegand, who used as the basic mixing one already containing litharge, was thus eliminated. In two instances, however, where barytes and zinc oxide were employed, an organic accelerator, thio-carbanilide, was included. The mixings were vulcanised, not for the same time in each case, but for the time so adjusted as to give the "best cure" at 140° C. The results for tensile strength were expressed in terms of the "tensile product" calculated on the actual rubber present, and not on the total cross-sectional area of the test-piece. In spite of the difference in the experimental technique, the results obtained by North were of the same order as those of Wiegand. Barytes again produced little effect on the form of the stress-strain curve; the extensibility actually increased slightly with additions up to 3 volumes per 100 volumes of rubber, whereas the tensile strength showed a speedy decline. The "corrected" tensile strength, or the tensile strength calculated on the rubber present, showed no alteration whatever with continued addition of barytes up to 50 volumes.

Lithopone also caused very little displacement of the curve, and very little alteration in the corrected tensile strength.

Up to addition of 15 volumes magnesium carbonate exhibited the best tensile properties, but with increasing additions the superiority of gas black became evident, zinc oxide being next in order of merit.

\* *I. R. W.*, 1920, 63, 98.

Measurements of permanent set were made, and up to 10 volumes the differences were not marked, but at 15 volumes and beyond magnesium carbonate caused very high set, gas black and zinc oxide exhibiting this behaviour in a lesser degree; lithopone and barytes produced least alteration in permanent set.

The results obtained by North confirm in a general way the conclusions of Wiegand regarding the beneficial influence of fineness of division of filling

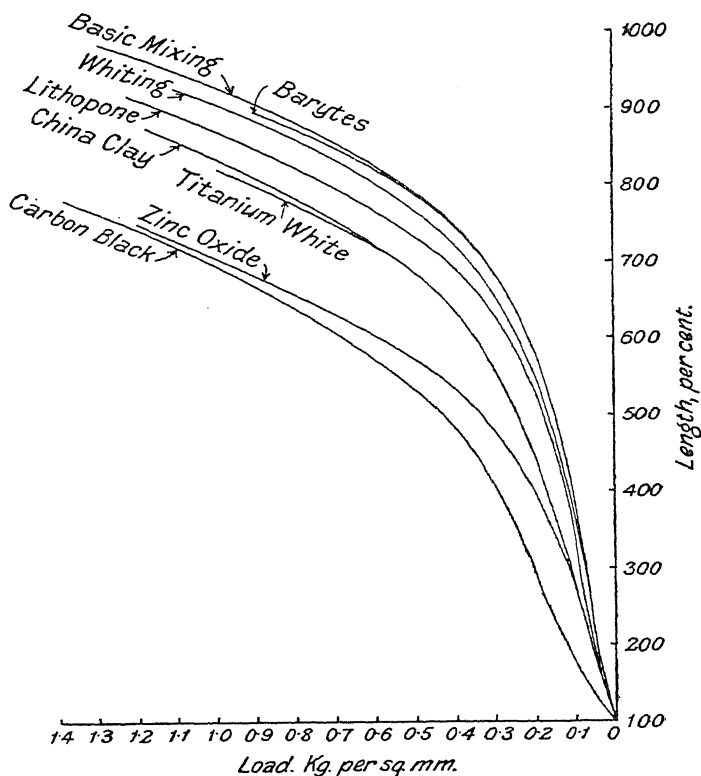


FIG. 7.

materials; direct experimental evidence is thus forthcoming in support of the supposed relationship between particular size of fillers and the tensile properties imparted to vulcanised rubber.

In the case of the fillers examined by Wiegand the basic mixing employed contained litharge, and the reinforcing effect may have been obscured in some cases; on the other hand, the experiments of North were complicated by vulcanising for different times in the several cases. A direct comparison of the reinforcing effect of different fillers is readily obtained by adopting as

basis mixing one containing rubber and sulphur only and heating for a definite time; any alteration in the position of the stress-strain curve will then be due to the influence of the particular filler. In experiments carried out in this way \* the mixing employed expressed on a volume basis was as follows :

Plantation Sheet	.	.	.	.	.	77.5 volumes
Sulphur	.	.	.	.	.	5.0 "
Filler	.	.	.	.	.	5.0 "

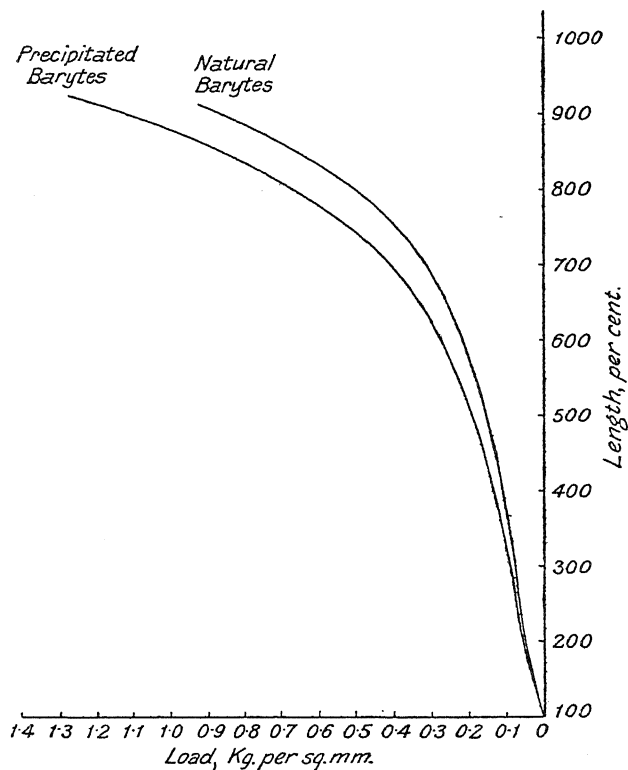


FIG. 8.

Mixings made up with a number of different fillers were vulcanised for 175 minutes at 141° C. and the stress-strain curves recorded by means of the Schopper machine. These are given in Fig. 7, and it will be noted that the superiority of carbon black is again evident; at the other extreme is barytes, which has produced very little alteration in the stress-strain curve. The relative particle size of the fillers employed may be gathered by an examination of the photo-micrographs, Plates 12a, 11b, 11a, of natural barytes, whiting and titanium

\* Private communication from E. Anderson and W. M. Ames.

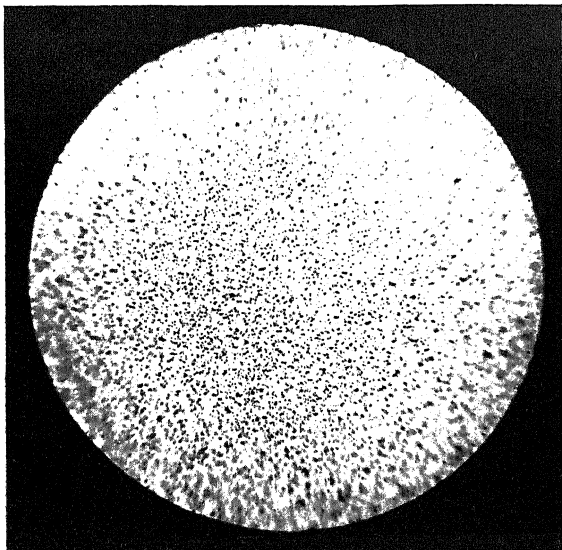


PLATE 11(A).—TITANIUM WHITE  $\times 600$ .

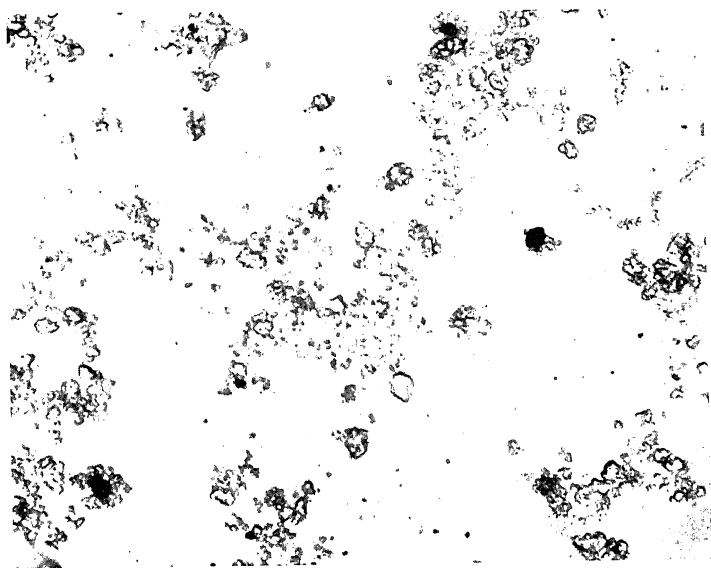


PLATE 11(B).—WHITING  $\times 350$ .

white respectively. It will be seen that, starting from the curve of the basic mixing, the downward order of the curves is in descending order of particle size, showing again the correlation between fineness of division of the filler and toughness of the vulcanised rubber.

Not only are differences of behaviour exhibited by different fillers, but, as might be conjectured, samples of the same filler may produce quite different effects due to variation in the particle size. This is especially marked when comparing a filler obtained by grinding a natural product with the substance of the same chemical composition obtained by a precipitation process. Stress-

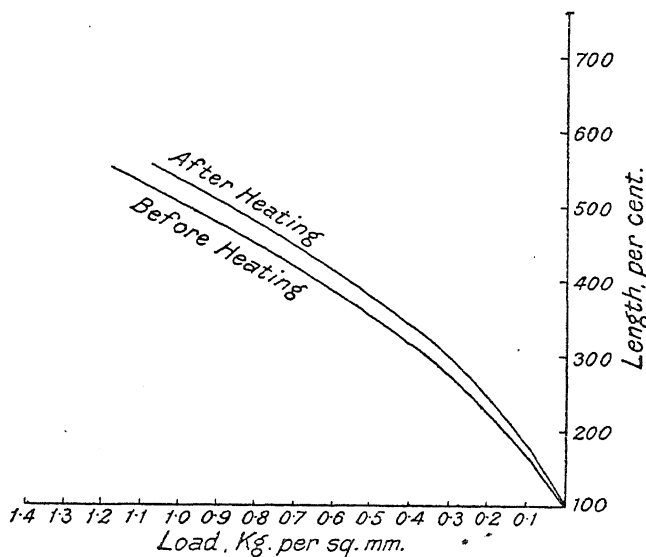


FIG. 9.

strain curves are given in Fig. 8 of similar mixings cured under the same conditions, one of which contained natural barytes, the other containing precipitated barium sulphate. Whereas natural barytes produced very little displacement of the stress-strain curve, it will be seen that the precipitated material caused a small but none the less definite movement towards the load axis.

Differences arising from variations in the method of preparation are well illustrated in the case of the forms of carbon at present in use. "Gas black," or, as it is sometimes called, "carbon black" is prepared by the incomplete combustion of natural gas, and is, on this account, deposited in a much finer state of division than is ordinary lamp black or vegetable black formed by the combustion of oils in a restricted air supply. The greater value of carbon black as a reinforcing filler was shown by the experiments of Wiegand, and this can

only be due to the difference in the specific surfaces of the two pigments. Another instance may be quoted in which the particle size was altered after formation. A sample of zinc-oxide was heated at about 700° C. and the tensile properties of mixings containing, on the one hand, the unheated sample, and, on the other, the sample after heating, were examined.

During the process of heating the reinforcing effect of the zinc oxide was partly destroyed, as illustrated by the stress-strain curve falling higher on the paper than in the case of the unheated sample (see Fig. 9). Photo-micrographs of the zinc oxide before and after heating are shown in Plates 16 and 17, and it will be seen at a glance that the heat treatment has caused an increase in particle size. This may be due, to some extent, to the zinc oxide possessing an appreciable vapour pressure at the temperature employed, resulting in the formation of crystals of larger dimensions than the original particles.

It was shown by Doeltz and Graumann \* that zinc oxide possesses an appreciable vapour pressure at temperatures in the neighbourhood of 1100° C., and at 1700° C. volatilises rapidly with formation of acicular crystals, examples of which may be seen in Plate 13a.

Enough has been said to indicate that as a general rule the more finely divided the filler the greater the resistance to extension and to rupture of the vulcanised rubber into which it is incorporated.

It appears logical to suppose that a definite mathematical relationship might be established whereby the tensile properties of any mixing could be predicted from a knowledge of the average particle size of the filler introduced.† There are, however, several factors which would tend to invalidate a calculation based on a determination of particle size alone.

In the first place, the measurement of the ultimate particular size cannot be performed with any degree of accuracy, and it is recognised that at any rate with the finer fillers the values obtained are only approximate. Some particles may be beyond the resolving power of an ordinary microscope, and with the visible particles it is often a matter of extreme difficulty to distinguish between individual particles and aggregates. Even if the particle size were known, the validity of any mathematical relationship would depend on whether or not the filler were dispersed to the maximum extent in the process of mixing with the rubber. The shape of the particle would almost certainly affect the resistance of the vulcanisate; a micro-crystalline substance like magnesium carbonate, for example, would behave differently from an amorphous powder of the same average particle size. It is not certain that even those fillers which are regarded as chemically inert may not be capable of exerting an influence on the progress

\* *Metallurgie*, 1906, 3, 212.

† Cf. Ames, *Rubber Age*, 1922, p. 213.

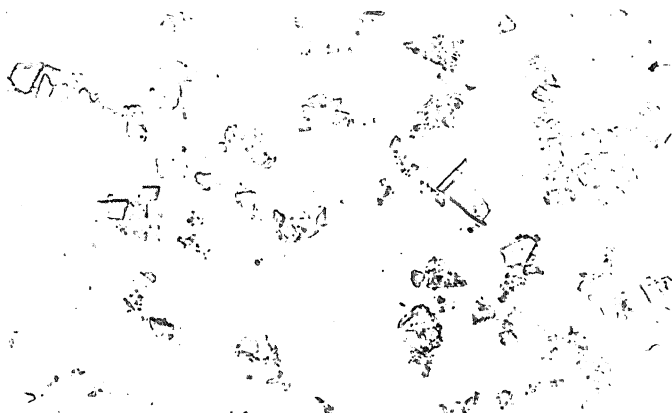


PLATE 12(A).—NATURAL BARYTES  $\times 350$ .

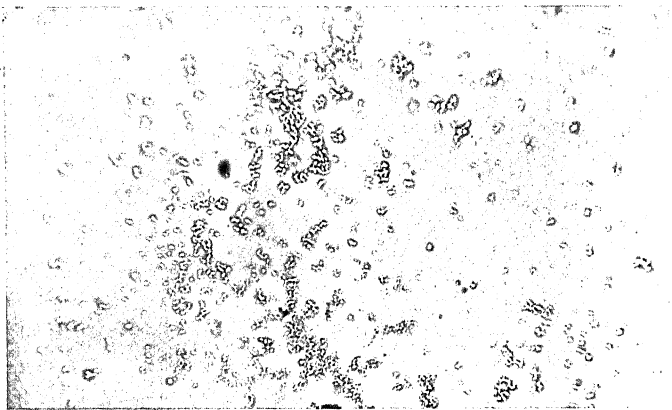


PLATE 12(B).—ZINC OXIDE, BEFORE HEATING,  $\times 700$ .

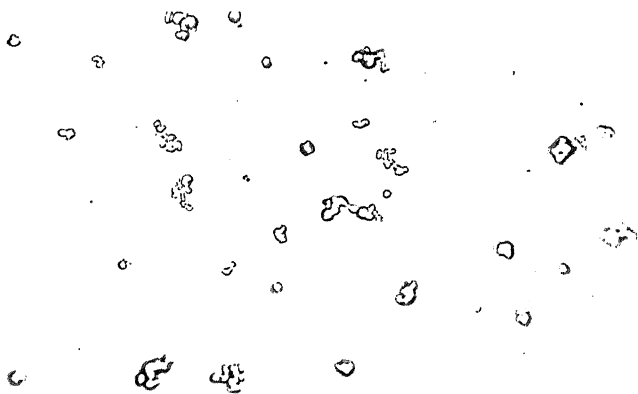


PLATE 12(C).—SAME ZINC OXIDE, AFTER HEATING,  $\times 700$ .



of vulcanisation quite apart from the effect due to close adhesion between their surface area exposed to the rubber. Thus, a catalysis of the purely chemical part of the vulcanisation process may conceivably occur in the case of some apparently inert fillers.

This was clearly illustrated in the case of two commercial samples of zinc oxide of different origin. Equal volumes of each sample were introduced into similar quantities of the same basic mixing, and the two lots vulcanised under the same conditions of time and temperature. The stress-strain curves

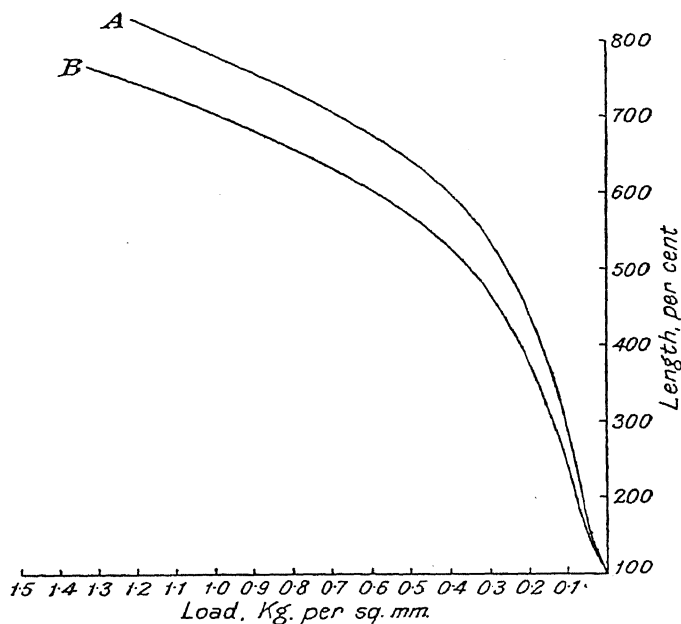


FIG. 10.

were obtained in the usual way, and are reproduced in Fig. 10; a marked difference in the tensile properties of the vulcanisates is noticeable. The percentage of combined sulphur was determined in each case at different times of cure, the following results being obtained :

Time of Vulcanisation @ 141° C.	Sample A.	Sample B.
120 minutes	1.14	1.71
140     "	1.42	1.85
180     "	1.71	2.12

The displacement of the stress-strain curve appears to have been due in the case of sample B to a combination of the influence of the finely divided pigment

acting as a reinforcing filler, and in addition as a catalyst of the vulcanisation process. No impurity could be detected which would be at all likely to accelerate in the one sample or retard, as would zinc sulphite, for instance, in the other sample. The proportion of sulphur fixed as zinc sulphide was determined, and in each case the figures were identical.

From the foregoing it is evident, therefore, that conclusions regarding the effect of a particular filler based on a consideration of particle size alone are apt to be misleading. Nevertheless, the researches of Wiegand afford a basis for investigating in a systematic manner the specific effect of the various compounding ingredients.

An example of this is seen in the work of Greider \* on light magnesium carbonate, which North (*loc. cit.*) had already shown to be a reinforcing filler. In view of the possibility of a shortage in the production of carbon black, owing to the sources of natural gas becoming diminished or exhausted, the supply of an alternative filler of this type becomes a matter of importance.

Greider adopted as the basic mixing one similar to that employed by Wiegand containing

Rubber	.	.	.	.	.	100 volumes
Litharge	.	.	.	.	.	3    ,,
Sulphur	.	.	.	.	.	2.3   ,,

Increasing volumes of light magnesium carbonate were added, and the mixings vulcanised at 143° C. for forty-five minutes. The effect of successive additions on the tensile and other properties of the vulcanised rubber was determined.

The tensile strength was found to increase up to 9 volumes of filler per 100 volumes of rubber, after which a falling off was noted, and after addition of 20 volumes the strength was equal to that of the basic mixing. The resilient energy calculated in the manner adopted by Wiegand increased to a maximum at 9 volumes of added filler, at which point the value corresponded to 149 per cent. of that exhibited by the basic mixing.

The resilient energy of the vulcanisates obtained after adding 9 volumes of other fillers was determined, and with this proportion the following values were obtained :

					Total Resilient Energy Foot-pounds/cub. inch.
Basic mixing	.	.	.	.	398
Addition of 9 volumes		magnesium carbonate	.	.	573
"	"	gas black	.	.	568
"	"	zinc oxide	.	.	513
"	"	china clay	.	.	500

\* J. I. E. C., 1922, 14, 385.

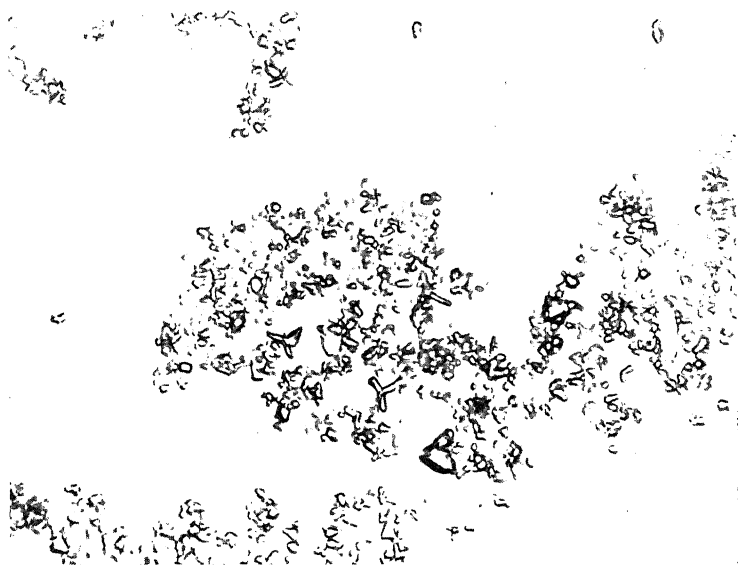


PLATE 13(A).—ZINC OXIDE  $\times 1200$ .



PLATE 13(B).—RUBBER MINING CONTAINING BARYTES  
UNDER STRAIN  $\times 380$ .

Up to the addition of 9 volumes per 100 volumes of rubber, therefore, magnesium carbonate is superior even to gas black as a reinforcing filler. The chief disadvantage in its use lies in the undesirably high permanent set imparted to the vulcanised rubber. Thus, with 20 volumes of magnesium carbonate the permanent set amounted to 30 per cent., against 16 per cent. produced with the same volume of gas black, and 14 per cent. given by zinc oxide.

This high permanent set is usually attributed to the definitely crystalline character of the magnesium carbonate. In the case of a vulcanised rubber containing such a crystalline filler the application of stress sufficient to produce a marked elongation tends towards the particles taking up an alignment with their long axes in the direction of the elongation. Under these circumstances the cohesion between the surface of the particle and the rubber is broken down, and on releasing the stress the particles cannot return to their original state of intimate contact with the rubber at the surfaces; consequently the rubber is prevented from regaining completely its original conformation. Greider points out that visible evidence of the displacement of the particles of magnesia is afforded by stretching a freshly vulcanised sample into which it has been incorporated with no other ingredient than sulphur. Such a sample is at first translucent, but when stretched becomes opaque, due to the changed refractive properties of the mass through loosening of the particles.

The interesting suggestion is made by Greider that by adjusting the conditions of precipitation in the preparation of magnesium carbonate it may be possible to subdue the crystalline character of the product and so to minimise the permanent set effect.

In connection with this supposed relation of permanent set to crystalline structure it may be pointed out that, as North (*loc. cit.*) has shown, ground natural barytes, which is markedly crystalline in character, does not exhibit this undesirable property. However, in this case, the crystals are of irregular shape owing to the effect of grinding, and probably on this account do not alter in position on stretching, as would crystals of a definitely acicular character.

#### AGEING PROPERTIES OF COMPOUNDED RUBBERS

The harmful influence of copper and manganese on rubber has been referred to in a previous chapter, and it is obvious that compounds containing these elements should be avoided as ingredients of vulcanised rubber mixings. Their presence as impurities in the various fillers is equally to be guarded against, otherwise the rubber will be liable to rapid deterioration. With very few exceptions the compounding ingredients commonly employed in rubber manufacture have been in use for a number of years, and consequently may be

said to have withstood the ordeal of practical tests extending over a long period. From the results of a series of experiments on accelerated ageing Evans \* concluded that a rapid deterioration was more frequently due to improper vulcanisation than to the specific effect of compounding ingredients present in the mixing. That differences in ageing properties may sometimes result from the use of different fillers has been shown by Anderson and Ames † in a comparison of the effects of antimony sulphide and iron oxide, both largely used red pigments, in a 90 : 10 rubber-sulphur mixing. Equal weights of the fillers were employed and each mixing cured for three different times. The breaking loads of the vulcanised samples are shown in Fig. 11, from which

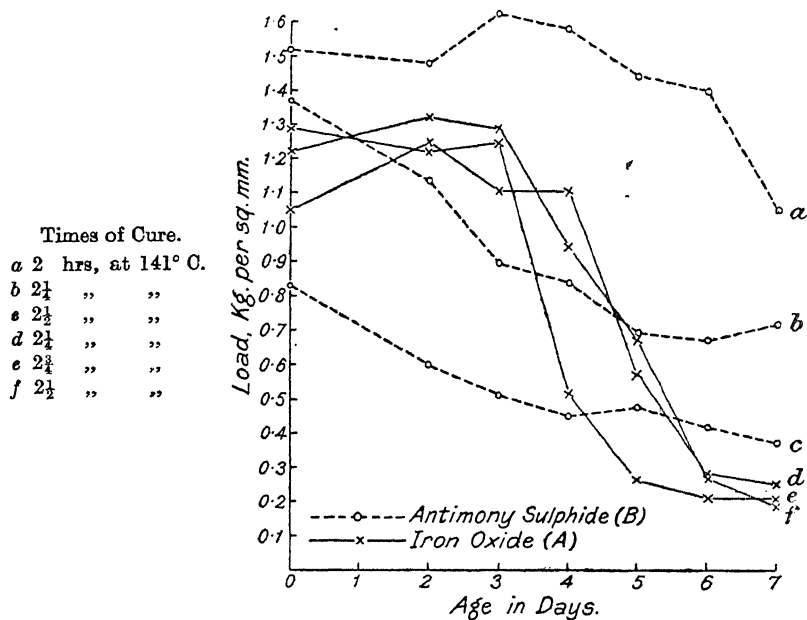


FIG. 11.

it is clear that the tensile properties of the antimony sulphide mixing are preserved for a much longer period than those of the iron oxide vulcanisate.

It may be remarked that the samples containing antimony sulphide were cured for a shorter time than the iron oxide mixing, but that this was not over-cured in any case is evident from the increase in tensile strength which took place in the early stages of the ageing period.

A comparison of the behaviour of rubber compounded with light magnesium carbonate and other fillers under the accelerated ageing test was made by Greider.† The results show that with nine volumes of filler per 100 volumes

\* *J. Amer. Soc. Testing Materials*, June 1922.† *J. S. C. I.*, 1923, 42, 136 T.‡ *J. I. E. C.*, 1922, 14, 392.

of rubber the best ageing was exhibited by the sample containing magnesium carbonate, the order of merit of the remainder being, zinc oxide, china clay, "colloidal" barium sulphate and gas black. The best results were obtained by the use of a mixture of equal proportions of magnesium carbonate and zinc oxide; in all these tests, however, the basic mixing contained litharge, and in the absence of added fillers did not itself show good ageing properties.

The incorporation of certain pigments, especially red or yellow ones, may exercise a beneficial influence on the lasting qualities of rubber goods. It has been shown that the oxidation of raw rubber takes place more rapidly in the presence of light, and the same is true of vulcanised rubber. The addition of a yellow pigment capable of absorbing the actinic rays was suggested by Henri \* as a means of prolonging the life of the rubber proofing on balloon fabric. The use of an oil soluble organic dye such as "Oil Red S." † has been found to give exceedingly good results in this connection, as the dye dissolves in the rubber, thereby affording complete protection from the effects of light. Carbon black is also valuable in this connection, as may be gathered from the results of some experiments carried out by the writer. Cloth proofed with a pure rubber-sulphur mixing was exposed, together with two similar samples, the proofing of one of which contained china clay, the other carbon black. After 110 days' exposure in the open the proofing on the carbon black sample was still supple, whereas in the other cases the rubber had almost completely perished and could be rubbed off in the form of powder. Extraction with acetone gave the following results :

Character of Mixing.	Acetone Extract (calculated on the rubber present).
Carbon black . . .	8.5 per cent.
China clay . . .	85.4 " "
Pure rubber . . .	96.3 " "

It is evident that the sample containing carbon black had not undergone appreciable decomposition even after long exposure to normal atmospheric conditions; a similar resistance was shown by a proofing containing vegetable black.‡

### REACTIONS OF COMPOUNDING INGREDIENTS DURING VULCANISATION

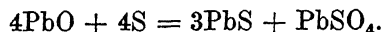
While the chemical process of vulcanisation is primarily one of combination of rubber with sulphur, subsidiary reactions between the sulphur and the

\* *Le Caout. et la G. P.*, 1910, 7, 4371.

† R. Wheatley and North British Rubber Co., Ltd., E.P. 5915, 1915.

‡ Hancock (*Personal Narrative*, p. 13) showed that by covering the surface of unvulcanised rubber with some black pigment, the harmful effect of exposure to sunlight was eliminated.

compounding ingredients may take place. This is especially likely to occur in the case of metallic oxides or hydroxides, the most notable example of which in this connection is litharge. The interaction of litharge and sulphur is evidenced by the colour of the mixing changing from yellow to black, due to the formation of lead sulphide according to the equation :



The effect of progressive additions of litharge to a mixture of rubber 100 parts, sulphur 5 parts by weight, has been studied by Stevens.\* Proportions varying from 0 to 70 parts of litharge were added and each mixing cured, in one case for two hours and in another case for three hours at 132° C. The sulphur present as lead sulphide after vulcanisation was determined as described on p. 220. In the sample vulcanised for two hours the proportion of sulphide sulphur gradually increased with addition of litharge from 0 to 2.57 per cent., calculated on the rubber present. The coefficient of vulcanisation with a cure of three hours increased from 1.86 in the sample containing no litharge to 3.37 when 17.5 parts of litharge had been added. With increasing proportions of litharge more sulphur entered into combination to form lead sulphide and lead sulphate, and consequently the proportion available for combining with the rubber was reduced. Thus the coefficient of vulcanisation diminished with addition of litharge in excess of 17.5 parts per 100 of rubber, until with 75 parts by weight of litharge the value obtained was only 1.31; the proportion of sulphur in combination with lead was then found to be 3.57 per cent. These figures show that where litharge is present the sulphur will tend to combine with the lead more readily than with the rubber, and the proportions of sulphur and litharge added must therefore be adjusted, so that the distribution of the sulphur between the rubber and the lead is such that there is available for combination with the rubber sufficient sulphur to ensure that vulcanisation will take place.

Apart from litharge the compounding ingredients in common use do not interact with sulphur to an appreciable extent. The writer has carried out experiments in order to ascertain the extent to which zinc oxide may react with sulphur during vulcanisation. Mixings containing varying proportions of zinc oxide and sulphur were vulcanised at 141° C. for the time necessary to give a technically cured vulcanisate. In another experiment a particular mixing was cured for different times in order to determine the influence of the time of heating on the combination. Determinations of sulphide sulphur were made by the method of Stevens, and the results are given in the following table :

\* *J. S. C. I.*, 1915, 34, 524.

	A.	B.	C.	D1.	D2.	D3.
Plantation Sheet .	80%	85%	57½%	55%	55%	55%
Zinc Oxide .	10	10	40	40	40	40
Sulphur .	10	5	2½	5	5	5
*Sulphide Sulphur	0.27	0.22	0.12	0.15	0.18	0.21
Time of Cure .	2½ hrs.	3 hrs.	3½ hrs.	2 hrs.	2½ hrs.	3 hrs.

\* Percentage calculated on the sample taken.

As will be seen from samples A, B, and C, the proportion of sulphur which enters into combination as zinc sulphide decreases with the proportion of sulphur relative to the zinc oxide present, even though the time of vulcanisation may be increased. That the proportion of sulphide sulphur formed in a particular mixing depends on the time of heating is seen from the results obtained with sample D, which showed a gradual increase in sulphur combined as sulphide with increasing time of cure.

The possibility of the sulphur interacting with the compounding ingredients was investigated by Ditmar and Thieben,\* who, instead of working with mixtures incorporated with rubber, heated together in an autoclave 10 gr. of each of the various fillers mixed with 2 gr. of sulphur for forty-five minutes at 4 atmospheres steam pressure. The reaction products were extracted with acetone and sulphur determined in the extract and in the residue. The following were the proportions of sulphur fixed by the respective fillers: magnesium carbonate, 7.2 per cent.; magnesium oxide, 80.5 per cent.; zinc oxide, 73.6 per cent.; barium sulphate, 62.33 per cent.; lead oxide, 66.06 per cent.; calcium carbonate, 76.20 per cent., calculated on the sulphur taken. These results, however, are not comparable with those obtained when the reaction takes place in a rubber medium. The figures are somewhat remarkable, since they show that a greater proportion of sulphur is fixed by zinc oxide than by litharge. It is difficult to understand how barium sulphate is to interact with sulphur, and certainly under normal vulcanising conditions the writer has never encountered more than a trace of sulphide sulphur in a mixing containing whiting; similarly, in experiments with both oxide and carbonate of magnesium, vulcanisation for a prolonged period failed to yield sulphides. In the vulcanisation of rubber mixings it is probable that the formation of metallic sulphides is not solely the result of interaction of the sulphur with the metallic oxide. It is known that the resins present in rubber, and perhaps also the nitrogenous constituent,

\* *Koll. Zeit.*, 1912, 11, 77.



react with sulphur to form hydrogen sulphide, which may then combine with the metallic oxide to form the sulphide.

It is possible, too, that in addition to reacting with sulphur, metallic oxides and hydroxides react during vulcanisation with the resinous or nitrogenous constituents. That a decomposition of the nitrogenous constituent may occur is readily proved by the formation of volatile bases in certain instances.

If a comminuted sample of a freshly vulcanised mixing containing litharge or calcined magnesia is placed in a stoppered tube, the presence of a volatile base may be detected by suspending a piece of red litmus paper in the air above the sample.

Even at comparatively low temperatures the formation of volatile bases has been ascertained. Thus, a mixture of rubber and litharge was sealed in a glass tube and heated for one hour in a steam bath at 100° C. alongside a sample of the uncompounded rubber similarly sealed; on opening the tube containing the litharge mixing a marked alkaline reaction could be detected, and that this was not due merely to a decomposition by heat of the nitrogenous constituent was shown by the fact that the rubber alone did not yield alkaline vapours.

#### VOLUME INCREASE OF COMPOUNDED RUBBER ON STRETCHING

Although a "pure" vulcanised rubber undergoes very little alteration in volume on stretching, a marked increase is noted in the case of rubber containing certain compounding ingredients. That a slight increase occurs even with a fairly pure rubber was demonstrated by Joule,\* who observed a reduction in the specific gravity of a rubber band after stretching. The circumstances under which compounded rubber increases in volume on stretching have been thoroughly investigated by Schippel,† who noted the change in specific gravity on stretching rings over a series of steel bars of varying lengths so as to obtain different degrees of extension.

A basic mixing of rubber 100, litharge 30, and sulphur 5 parts by weight was adopted, and to this increasing volumes of different compounding ingredients added. The samples were vulcanised to give rings of a cross-sectional diameter of  $\frac{1}{2}$  inch, and an exterior diameter of  $2\frac{1}{4}$  inches, which were then examined as described. The increase in volume at different elongations was determined with each proportion of filler added. The results showed that, as a general rule, for a given proportion of filler the increase in volume became greater as the extension of the rubber was increased. Similarly, for a given extension the volume increase rose with increasing proportions of filler. With

\* *Phil. Trans.*, 1859, **149**, 104.

† *J. I. E. C.*, 1920, **12**, 33.

coarse fillers, such as barytes, the increase in volume at a given elongation rose uniformly with increase in the proportion of filler. With the finer pigments, such as carbon black or zinc oxide, the increase in volume was small with proportions of filler up to about 30 volumes per 100 of basic mixing, but after this suddenly rose. The explanation of this phenomenon offered by Schippel is that on extending rubber containing large particles of filler, vacuoles are formed at the ends of the particle in the direction of the stretch. With comparatively low proportions of finely divided fillers the adhesion between the rubber and the particle does not allow of the formation of vacuoles. With higher proportions of fillers the rubber no longer completely "wets" the particles, under which circumstances aggregates are formed which give rise to the vacuoles. In support of this theory an experiment was described in which lead shot was introduced into a transparent rubber mixing which, on stretching, exhibited vacuoles at the poles of each individual shot. The percentage increase in volume observed on stretching to 200 per cent. elongation samples of vulcanised mixings containing 20 volumes of several fillers is indicated in the following table : \*

Filler.	Apparent Specific Surface.	Volume increase at 200% elongation.
Carbon black . . . . .	1,905,000	1.46
Lamp black . . . . .	1,524,000	1.76
Iron oxide . . . . .	152,400	1.9
Zinc oxide . . . . .	152,400	0.8
Whiting . . . . .	60,390	4.6
Barytes . . . . .	30,480	13.3

The results indicate that the greater the particle size of the pigment, and therefore the smaller the specific surface, the greater will be the increase in volume observed under comparable conditions.

A simple experiment to illustrate the volume increase on stretching has been described by Schippel.† A ring of compounded vulcanised rubber is stretched over an elongated plug of paraffin wax, the size of which is adjusted so that the combination just floats in water. If the ring is now removed and attached to the narrow portion of the plug, so that the strain is removed, the combination will be found to sink in water due to the contraction of the vacuoles, with a consequent decrease in volume and increase in specific gravity of the system. The production of vacuoles in compounded rubber under strain has been

\* Wiegand, *J. I. E. C.*, 1921, 13, 124.

† *I. R. W.*, 1919, 61, 20.

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demonstrated microscopically in the case of a barytes mixing by Green,\* who succeeded in obtaining photomicrographs of a section while in a state of tension, the vacuoles being clearly discernible. Similar photomicrographs have been obtained by Ames (private communication), the vacuoles at the poles of the particles of barytes, and of aggregates of whiting and of "free" sulphur, being shown in Plates 13*b*, 14*a*, and 14*b*.

\* *J. I. E. C.*, 1921, 13, 1029.



PLATE 14(A).—WHITING IN MIXING UNDER STRAIN  $\times 440$ .



PLATE 14(B).—FREE SULPHUR IN MIXING UNDER STRAIN  $\times 1000$ .

## CHAPTER XII

### ACCELERATORS

#### INORGANIC ACCELERATORS

It has been known for some considerable time that certain inorganic compounds, such as litharge, magnesium oxide and calcium oxide or hydroxide, when added to a mixture of rubber and sulphur, effect a reduction in the time necessary for the characteristics of vulcanisation to be assumed. Latterly it has been found that a similar result is obtained by the use of other substances, such as caustic soda, and in general sodium salts of weak acids, by ammonium carbonate, antimony sulphide and others.

Probably the most extensively used inorganic accelerator is lead monoxide, which appears on the market either as the reddish-yellow litharge or the canary-yellow massicot.

The extent to which the addition of either of these forms will influence the progress of vulcanisation may be gathered from a consideration of a specific example. A mixture of  $92\frac{1}{2}$  parts of rubber with  $7\frac{1}{2}$  parts of sulphur when press-cured in a mould is vulcanised in, say, 200 minutes at  $140^{\circ}$  C. The addition of 10 parts of litharge to 100 parts of the same mixing would reduce the time of vulcanisation to 30 minutes at  $140^{\circ}$  C.

At one time the effect of litharge was attributed to its high thermal conductivity allowing the heat to be more quickly distributed to the rubber, but Seidl \* showed that although zinc oxide possessed equally high conductivity the accelerating effect was negligible. As a result of experiments with mixings containing extracted and unextracted rubber, Seidl † concluded that the effect was due to the rise in temperature occasioned by the reaction between the rubber resins and sulphur, which in the presence of litharge proceeded with greater vigour. Mixings were made up with (a) Para rubber, (b) Para rubber extracted with acetone, (c) the same as (b) but with addition of the oily product obtained by the destructive distillation of blood albumen, and (d) Para rubber extracted with acetone and purified by dissolving in petroleum ether and precipitating with alcohol. Each of these mixings was then wrapped round a

\* *Gummi Zeit.*, 1911, 25, 710.

† *Ibid.*, p. 748.

thermometer and immersed in an oil bath heated to  $140^{\circ}\text{C}$ ., when it was found that in the cases of (a), (b) and (c) the temperature rose above that of the bath, being highest in (a) and lowest in (b); very little rise in temperature, however, occurred in the case of (d).

Samples of the same mixing cured in a press for the same time gave vulcanisation coefficients as follows : (a) 2.42, (b) 1.73 and (c) 2.06. The combined sulphur here probably included the sulphur in combination as lead sulphide, but the figures indicate that the reaction had progressed farthest in the sample containing the original resins and least of all in the acetone-extracted sample. According to Seidl, therefore, the effect of litharge consists in raising the temperature of the mass over that of the heating medium, so that instead of the vulcanisation taking place at the temperature of the heating surface or atmosphere, it really occurs at a higher temperature. Considering that the temperature coefficient of vulcanisation is approximately 2.5 for  $10^{\circ}\text{C}$ ., a reduction in time to 40 per cent. of the original must be accompanied by a rise in temperature of  $10^{\circ}$  within the rubber mixing. If this were the case comparatively thick sheets of rubber vulcanised in moulds should be cured to a much greater extent in the interior than at the outside surface, which, being in contact with the metal mould, should retain approximately the same temperature as the press plate or other source of heat. On the other hand, in the case of thin sheet cured in a press the excess heat would be conducted to the press plate and a rise in temperature of the necessary magnitude could not well occur. While it is hardly likely that the explanation offered by Seidl is entirely correct, the fact that the natural rubber resin plays a part in the process of acceleration by litharge has been amply demonstrated by L. E. Weber and by Stevens. Weber \* found that rubber extracted with acetone when mixed with litharge, whiting and sulphur did not yield a satisfactorily vulcanised product, judged by tensile properties, as did the original rubber or the original rubber with added resins. Stevens † showed that not only did extracted rubber vulcanise slowly in presence of litharge, as evidenced by the tensile properties of the vulcanisate, but that the coefficient of vulcanisation was lowest in the case of extracted rubber and highest in the case of rubber to which additional resin had been added. In the results obtained by Stevens the vulcanisation coefficient was calculated after allowing for the sulphur present in combination with the lead as sulphide and sulphate.

The chief value of litharge lies in the fact that rubber-sulphur mixings in which it is incorporated may be vulcanised simply by exposing to a heated

\* *Int. Cong. Appl. Chem.*, 1912, 9, 95.

† *J. S. C. I.*, 1916, 35, 874.

atmosphere at ordinary pressures. In the absence of litharge and of certain organic accelerators satisfactory vulcanisation is accomplished only by heating under pressure either in a mould between the plates of a press or in an autoclave fed with live steam under pressure, in which case the sample may be exposed directly to the steam or may be protected either by a cloth wrapping or by embedding in some powder such as French chalk. The function of litharge in expediting the process of vulcanisation at ordinary atmospheric pressure is not clear, but is usually attributed to the protection afforded against the effect of atmospheric oxygen, which would tend to render the surface of the goods tacky. On the assumption that a reducing agent would exert a similar influence, the use of reducing agents such as sulphites and certain formaldehyde derivatives or of certain readily oxidisable phenols, such as pyrogallol or *p*-aminophenol has been suggested,\* but these do not entirely prevent the development of surface tackiness.

While litharge is the most active of the compounds of lead, it would be expected that others containing lead oxide or hydroxide would act in a similar manner to litharge.

That this is the case has been shown by Grove † in an examination of the relative activity of litharge, basic lead carbonate, sublimed white lead (basic lead sulphate) and sublimed blue lead (an impure form of basic lead sulphate containing lead sulphide). A determination was made of the proportions of the lead compound necessary to produce the same degree of acceleration of the cure of a mixing containing rubber 80, sulphur  $2\frac{1}{2}$ , zinc oxide 5 parts by weight, the difference between the total and 100 parts being made up with the lead compound and barytes. The relative amounts of the lead compounds added to produce the same result in each case were litharge 1, basic lead carbonate 3, sublimed white lead 3, sublimed blue lead 7.

In order to secure a more homogeneous admixture of lead compound with the rubber, the oleate has been employed in America, or the oleic acid may be added to a litharge-containing mixing.‡

Calcined magnesia,  $MgO$ , is a very effective accelerator, 1 part by weight added to 100 parts of 90 : 10 rubber-sulphur mixing reducing the time of cure approximately to the same extent as would 10 parts of litharge. An idea of the relative accelerating effects of litharge and calcined magnesia may be gathered from the results obtained by Stevens,§ showing the increase in vulcanisation coefficient produced by successive additions of either ingredient to

\* Helbronner, E.P., 142083.

† L. E. Weber, *I. R. J.*, 1922, **63**, 793.

‡ *I. R. W.*, 1921, **64**, 663.

§ *J. S. C. I.*, 1918, **47**, 156 T.

a mixture of 90 parts by weight of rubber and 10 parts of sulphur, and heating in steam for one hour at 138° C.

Litharge. <sup>1</sup>	Coefficient.	Magnesia. <sup>1</sup>	Coefficient.
—	1.26	—	1.40
0.1	1.25	0.1	2.66
0.25	1.27	0.25	3.31
0.5	1.37	0.4	3.68
0.8	1.75	0.75	4.08

<sup>1</sup> Parts added per 100 of basic mixing.

These figures show clearly that in small proportions litharge produces very little acceleration of the vulcanisation reaction as compared with calcined magnesia. Like litharge, magnesia appears to depend upon the presence of acetone soluble material in the rubber for the attainment of the maximum effect.\*

Basic magnesium carbonate, which is largely used in rubber manufacture, is of variable composition, generally expressed by the formula  $4\text{MgCO}_3, \text{Mg}(\text{OH})_2, 5\text{H}_2\text{O}$ ; according to Greider,† however, analyses more nearly correspond to the formula  $11\text{MgCO}_3, 3\text{Mg}(\text{OH})_2, 11\text{H}_2\text{O}$ , but the composition may be influenced by the temperature at which precipitation takes place.

Magnesium carbonate, while of more interest as a reinforcing filler (see p. 162), functions as a mild accelerator, although in this respect it is very much less active than magnesium oxide, and is indeed inferior to litharge.

Sodium hydroxide is a very active accelerator, a fact which was first established by Martin,‡ who showed that even with very small proportions a noticeable reduction in the time of cure was effected. Working with a mixing of Para rubber 38½ per cent., zinc oxide 60 per cent., sulphur 1½ per cent., it was found that on the addition of caustic soda in proportions up to 0.5 per cent. the acceleration effect increased progressively. Higher proportions caused a gradual retardation of the cure, until with 5 per cent. added the mixing could not be satisfactorily vulcanised. This may have been due partly to the interaction of the sodium hydroxide with a proportion of the sulphur, leaving insufficient available for vulcanisation. As Martin has pointed out, the

\* Kratz and Flower, *J. I. E. C.*, 1920, 12, 971.

† *J. I. E. C.*, 1922, 14, 385.

‡ *Rubber Industry*, 1914, p. 205.



accelerating action of sodium hydroxide may be responsible for variations observed in the vulcanisation of mixings containing reclaimed rubber made by the alkali process, since, if the washing after treatment with alkali is incomplete, the product will impart a higher rate of cure to the stock into which it is introduced.

In order to secure a more uniform distribution of the alkali throughout the rubber, it has been proposed first to dissolve the caustic soda in some organic liquid or to form a salt with a weak organic acid. For example, glycerol may be employed as a suitable vehicle,\* and other hydroxylic derivatives, such as alcohols or phenols, may be used to dissolve the caustic soda; † alternatively a sodium derivative of a phenol such as sodium phenoxide may be added in solid form.‡ Other sodium salts, such as the carbonate, silicate, oleate, and in fact most sodium salts of weak acids, are effective as accelerators.

Ammonia functions as a mild accelerator, and as long ago as 1881 Rowley devised a method of vulcanisation in which the rubber and sulphur mixing was heated in an autoclave in the presence of ammonia or of substances capable of yielding ammonia on heating.

Among other inorganic compounds which accelerate the vulcanisation process are arsenic trisulphide,§ antimony sulphide || and polysulphides, such as zinc persulphides.¶

## ORGANIC ACCELERATORS

While the extensive employment of organic accelerators in rubber manufacture may be said to date from the year 1914, it has been stated that the incorporation of organic substances such as aniline for the specific purpose of hastening the process of vulcanisation was practised in America as early as 1906, and that in 1907 thiocarbanilide, which later found wide application, was introduced by Oenslager.\*\* Spence, too, has claimed that the "quicker curing mixing which . . . contained about 9 per cent. of sulphur and was free from mineral compounds," and which was referred to in a paper published in 1912,†† actually contained piperidine.

The first public disclosure of the use of an organic compound as an accelerator of vulcanisation was, however, contained in the Bayer patent of 1913,‡‡

\* Dunlop Rubber Co. and Twiss, E.P. 17756, 1916.

† North British Rubber Co. and Porritt, E.P. 129798.

|| Anderson and Ames, *J. S. C. I.*, 1923, **42**, 136 T.

\*\* Cf. W. C. Geer, *J. I. E. C.*, 1922, **14**, 372.

‡‡ E.P. 11530, 1913.

† *Ibid.*, E.P. 125696.

§ Twiss, *I. R. J.*, 1923, **65**, 696.

¶ *J. I. E. C.*, 1922, **14**, 29.

†† *Koll. Zeit.*, 1912, **10**, 303.



later nitrosobenzene, a compound which does not contain an amino-group, was shown to act in a similar manner.\* It has further been proved that nitrogen is not necessarily a constituent of an organic accelerator, since certain xanthates and dithio acids have been found to possess considerable activity. Nevertheless, the claim embodied in the Bayer patent does not seem to have been invalidated, since there is no record of a substance having a dissociation constant higher than  $1 \times 10^{-8}$  having been found not to possess the property of accelerating vulcanisation. While the number of individual organic accelerators which have been adopted or proposed must now be numbered by the hundred, they fall into fairly well-defined classes, which may be briefly enumerated.

### NITROGENOUS ACCELERATORS

*Ammonia derivatives of aldehydes.*—Hexamethylenetetramine (also known as H.M.T., Hexamine, or Hex),  $C_6H_{12}N_4$ , from formaldehyde; Aldehyde Ammonia, from acetaldehyde; Furfuramide (Vulcazol), from furfural; Hydrobenzamide, from benzaldehyde.

*Aliphatic Amines.*—Piperidine.

*Carbon disulphide derivatives.*—The interaction of primary or secondary aliphatic amines with carbon disulphide yields the salt of the amine with the corresponding dithiocarbamic acid, Piperidine pentamethylene dithiocarbamate; Dimethylamine dimethyldithiocarbamate.

*Aldehyde derivatives.*—Benzylidene ethylamine (Benzaethylamine)  $C_6H_5 \cdot CH:N(C_2H_5)$ .

*Aromatic Amines.*—Aniline; Monomethylaniline, Dimethylaniline; Toluidine; Phenylenediamine; Dimethyl-*p*-phenylenediamine; Diphenylamine; Aminophenol.

*Derivatives with aldehydes.*—Anhydroformaldehyde aniline (Methylene aniline),  $C_6H_5N:CH_2$ ; Methylenediphenyldiamine,  $CH(NC_6H_5)_2$  (from one molecule formaldehyde and two molecules aniline); Benzylidene aniline (Benzalaniline),  $C_6H_5 \cdot CH:N \cdot C_6H_5$ .

*Derivatives with carbon disulphide.*—In this way are formed substituted thioureas, as, for example, Thiocarbanilide (diphenylthiourea), sym.-di-*o*-tolyl thiocarbamide.

*Guanidines.*—Monophenylguanidine; Diphenylguanidine; sym.-Triphenylguanidine.

*Nitroso-derivatives.*—*p*-Nitrosodimethylaniline ("Accelerene"), *p*-Nitrosodiphenylamine, *p*-Nitrosobenzene, *p*-Nitrosophenol.

*Alkaloids*.—Brucine, Narcotine, Quinoidine.

*Thiouram disulphides*.—Formed by treating dithiocarbamates with mild oxidising agents or with halogens :

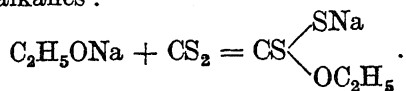


Examples are tetramethylthiouram disulphide,  $\text{N}(\text{CH}_3)_2\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{N}(\text{CH}_3)_2$ ; dipentamethylenethiouram disulphide,  $(\text{C}_5\text{H}_{10})\text{N}\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{N}(\text{C}_5\text{H}_{10})$  (from the reaction product of piperidine and carbon disulphide).

Among other types of substances which have been found to possess the property of accelerating vulcanisation may be mentioned the colour bases of basic dyestuffs which sometimes impart a distinctive colour to the vulcanised rubber \*—phenylhydroxylamine, benzene sulphonamide and carbothialdine (the product of the reaction of carbon disulphide with aldehyde ammonia).

### NON-NITROGENOUS ACCELERATORS

*Xanthates*.—The most important class of accelerators which do not contain nitrogen are the xanthates formed by the interaction of carbon disulphide and alcoholic solutions of alkalis :



The sodium, potassium, zinc, and lead salts are all active accelerators in presence of zinc oxide.

Other non-nitrogenous accelerators are anthraquinone, benzoquinone (more particularly in connection with the Peachey Vulcanisation Process), and salts of dithio acids,† as, for example, the zinc salts of dithiobenzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CSSH}$ , and also the corresponding disulphides, as dithiobenzoyl disulphide,  $\text{C}_6\text{H}_5\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{C}_6\text{H}_5$ .

### UTILITY OF ACCELERATORS

By the introduction of accelerators into a mixture of rubber, sulphur and compounding ingredients, the time of heating necessary for the development of the characteristics of vulcanisation is reduced. This alone would offer considerable advantages to the manufacturer, since the capacity of a given vulcanising plant could thereby be greatly increased. There are, however, other directions in which the use of accelerators may prove beneficial, and in certain instances they are employed without regard to the reduction of time

\* Gaisman and Rosenbaum, E.P. 141412.

† Bruni, *I. R. J.*, 1922, 64, 937; Romani, *Le Caout. et la G. P.*, 1922, 19, 11,626.

of cure. For example, not only is it possible to effect vulcanisation in a shorter time, but also at a lower temperature, a circumstance which allows of the introduction of colouring materials which are unstable under normal vulcanising conditions. Again, in the presence of accelerators vulcanisation proceeds with a lower proportion of added sulphur than would otherwise be required; less free sulphur will thus remain in the finished article, which will consequently exhibit less tendency to "blooming." Further, the tensile properties of vulcanised rubber made with an accelerated mixing are generally superior to those of the same mixing cured without an accelerator.

### RELATIVE ACTIVITY OF ACCELERATORS

As perhaps might be expected, the activity of the different accelerators varies considerably; not only is this the case, but a particular accelerator may prove more effective in presence of certain compounding ingredients than in their absence. The most notable instance of this behaviour is exemplified in the activating influence of zinc oxide. The fact that certain accelerators attain their maximum activity only in the presence of zinc oxide was established some time ago, but there does not seem to be any definite pronouncement relative to its discovery. It is quite likely that the introduction of zinc oxide into an accelerated mixing arose from a desire to provide a neutral or non-acid medium for the development of the full activity of the basic organic substances first employed. Apart from this consideration, the value of an accelerator would depend on whether it could be used with advantage in compounded as well as uncompounded mixings, the majority of which contain zinc oxide. It thus became a recognised part of laboratory procedure to test the activity of accelerators not only in pure rubber sulphur mixings, but also in those containing zinc oxide. Definite mention of this behaviour appears to have been first made in 1919 by Cranor,\* who, working with a variety of mixings containing accelerators, included 1 per cent. of this filler in order that the best results might be obtained "with accelerators which exert a maximum effect only when used in the presence of zinc oxide."

The effect of even small proportions of zinc oxide may be gathered from the results obtained by Twiss and his collaborators. Thus the addition of  $\frac{1}{2}$  per cent. of hexamethylenetetramine to a standard 90 : 10 rubber-sulphur mixing was shown to reduce the time necessary for the attainment of maximum tensile strength from 80 to 70 minutes; in the presence of 1 per cent. of zinc oxide the time was reduced to 40 minutes.† Thiocarbanilide is dependent to

\* *I. R. J.*, 1919, 63, 1199.

† Twiss and Brazier, *J. S. C. I.*, 1920, 39, 130 T.

a much greater extent on the presence of zinc oxide, and is in fact almost inactive in mixings which do not contain this ingredient.\*

The activating effect is very marked in the case of the dithiocarbamates, as, for example, the piperidine salt of pentamethylenedithiocarbamic acid. A 90 : 10 rubber-sulphur mixing containing 0.25 per cent. was found to attain maximum tensile strength in approximately 200 minutes at 128° C.; addition of 1 per cent. of zinc oxide reduced this time to 20 minutes, whilst in the presence of 5 per cent. zinc oxide an even shorter time sufficed.†

Other dithiocarbamates show similar behaviour, and in fact it has been reported by Tuttle ‡ that the addition of 0.1 per cent. of dimethylamine dimethyldithiocarbamate to a 90 : 10 rubber sulphur mixing which does not contain zinc oxide actually retards vulcanisation. This statement, however, is not borne out by the experiments of Bean,§ who found that even in the absence of zinc oxide a positive though small reduction in the time of cure was effected. Thiouram disulphides, zinc ethyl xanthate and the zinc salts of the dithiocarbamates are all activated to a marked extent by the presence of zinc oxide. In mixings which do not contain zinc oxide they would possess little interest as accelerators, whereas in presence of zinc oxide their activity is such that the term "ultra-accelerators" has been applied to them.|| In comparing the effectiveness of accelerators it is evident, therefore, that the composition of the basic mixing should be chosen so as to allow of the full development of their activity.

The comparison of accelerators is usually accomplished by introducing varying proportions into one or more basic mixings and noting the time taken for the attainment of a standard degree of vulcanisation. This may be based on a consideration of the coefficient of vulcanisation, or a definite physical standard may be adopted. In the latter case the attainment of maximum tensile strength or of a fixed degree of extensibility may be chosen as the criterion; the extensibility may be determined by the elongation at a given load or by the load necessary to produce a given elongation. Various methods have been adopted for expressing numerically the relative activity of accelerators. For example, Kratz, Flower and Coolidge ¶ determine the "excess sulphur coefficient," or the increase in the coefficient of vulcanisation of a mixing containing a standard proportion of accelerator over that of the basic mixing vulcanised under the same conditions. Alternatively, they find the

\* Twiss, Brazier and Thomas, *J. S. C. I.*, 1922, **41**, 83 T.; Whitby and Walker, *J. I. E. C.*, 1921, **13**, 818.

† Twiss, Brazier and Thomas, *J. S. C. I.*, 1922, **41**, 81.

‡ *J. I. E. C.*, 1921, **13**, 521.

|| Bruni, *ibid.*, 1921, **63**, 64.

§ *I. R. J.*, 1922, **63**, 354.

¶ *J. I. E. C.*, 1920, **12**, 322.

amount of accelerator necessary to add in order to produce the same physical properties as are given by a fixed amount of a standard accelerator, aniline. Thus in a "pure" rubber-sulphur mixing (92.5 : 7.5) vulcanised at 148° C. to give a "correctly cured" product in 90 minutes, the following proportions of accelerators were employed :

Aniline . . . . .	1.000
Urea . . . . .	0.250
Thiourea . . . . .	0.300
Monophenylthiourea . . . . .	0.450
Diphenylthiourea . . . . .	0.850
Monophenylguanidine . . . . .	0.075
Diphenylguanidine (Sym.) . . . . .	0.075
Triphenylguanidine . . . . .	0.500
Anhydroformaldehyde aniline . . . . .	0.750
<i>p</i> -Phenylenediamine . . . . .	0.170
Monoanhydroformaldehyde <i>p</i> -phenylenediamine . . . . .	0.140
Dianhydroformaldehyde <i>p</i> -phenylenediamine . . . . .	0.140

From the above it will be seen that the accelerators differ widely in activity, the amount necessary to produce a given physical effect varying from 0.075 in the case of mono- and diphenylguanidine to 1.000 in the case of aniline. While this method admits of a comparison of the relative accelerating action, it does not indicate the actual reduction in time of the process of vulcanisation.

The use of an "acceleration factor" as adopted by Twiss and Brazier\* indicates clearly the reduction in time effected by the addition of the accelerator. This factor is simply the ratio of the time taken to attain a definite degree of vulcanisation in a standard mixing to the time in which vulcanisation is effected after addition of the accelerator. Thus an accelerator which in a given proportion, say 1 per cent., reduces the time of cure of a standard mixing from 200 to 50 minutes would be described as possessing an "acceleration factor" of 4 for an addition of 1 per cent. Although this factor may differ according to the particular vulcanisation standard adopted, it will not vary to an appreciable extent at different temperatures, Twiss and Brazier having shown that as a general rule the temperature coefficient of the reaction velocity for an accelerated mixing is of approximately the same order as that for a simple rubber-sulphur mixing. The temperature coefficient for a 90 : 10 rubber-sulphur mixing was found to be 2.3 for a rise of 10° C. between 128° and 168° C.; for the same mixing with  $\frac{1}{2}$ ,  $\frac{1}{4}$ , and  $\frac{1}{8}$  per cent. aldehyde ammonia, the average value of the coefficient between 118° C. and 148° C. was found to

\* J. S. C. I., 1920, 39, 129 T.

be 2.3, 2.4 and 2.3 respectively. Thus the relative effectiveness of different accelerators should be the same for any temperature within the usual limits; this was found not to hold good for temperatures below 108° C., and this is explained by assuming that just below this temperature the sulphur in contact with accelerator, rubber resins, etc., melts and the reaction velocity is thereby enhanced. A further method of expressing the acceleration effect is that employed by Anderson and Ames,\* who record the "percentage acceleration," or the reduction in time effected by the introduction of the accelerator expressed as a percentage of the time of cure of the original mixing. Thus, a certain percentage of accelerator causing a reduction in the time of cure from 200 to 50 minutes would be said to effect an acceleration of  $200 - 50 = 150$  minutes, or 75 per cent.

Although a considerable volume of work has been published relating to the activity of various accelerators under different conditions, the lack of uniformity of the methods adopted renders an exact comparison a matter of extreme difficulty. Thus, whereas several workers employ as standard a mixing containing 90 parts of rubber and 10 parts of sulphur, others employ lower proportions of sulphur corresponding more nearly with what would be met with under manufacturing conditions. In some cases the percentage of combined sulphur is taken as the criterion of vulcanisation, in others the attainment of maximum tensile strength, and frequently the point at which a given load produces a definite elongation. Nevertheless, a general idea may be gathered of the relative activity of the various classes of accelerators more commonly employed.

The greatest activity is undoubtedly exhibited by the dithiocarbamates and the closely related thiouram disulphides, both types being dependent on the presence of zinc oxide for the attainment of maximum activity. For example, Twiss, Brazier & Thomas † have shown that in the absence of zinc oxide the acceleration factor for 1 per cent. of the piperidine pentamethylene dithiocarbamate in a 90 : 10 rubber-sulphur mixing is 7.7, whereas in the presence of 20 per cent. zinc oxide the factor for only  $\frac{1}{4}$  per cent. of the accelerator is greater than 100, which is equivalent to more than 300 for 1 per cent. of the dithiocarbamate.

For aldehyde ammonia the factor for  $\frac{1}{4}$  per cent. accelerator in a similar mixing is approximately 4, and in this case the activity is not influenced appreciably by the presence of zinc oxide.

Thiocarbanilide in the absence of zinc oxide produces an extremely small acceleration when judged by the physical properties of the vulcanisate, although

\* *J. S. C. I.*, 1923, **42**, 137 T.

† *Ibid.*, 1922, **41**, 81 T.



a marked increase in the coefficient of vulcanisation is noted.\* In the presence of only 1 per cent. of zinc oxide, however, the acceleration factor for 1 per cent. in a 90 : 10 rubber-sulphur mixing is in the neighbourhood of 2.†

Hexamethylenetetramine in presence of zinc oxide is intermediate in activity between thiocarbanilide and aldehyde ammonia; in a 90 : 10 rubber-sulphur mixing the acceleration factor for  $\frac{1}{2}$  per cent. is approximately of the same order as that for  $\frac{1}{4}$  per cent. of aldehyde ammonia. In the absence of zinc oxide the acceleration produced is relatively small.

Attempts have frequently been made to correlate chemical and physical properties of compounds with their activity as accelerators.

The possible connection between basicity and accelerating power was investigated by Kratz, Flower and Shapiro,‡ who found that, judging by the effect on the coefficient of vulcanisation, the activity did not vary in proportion to the dissociation constant.

A number of amino-compounds were examined in a 100 : 8.1 rubber-sulphur mixing, gram-molecular proportions being added instead of equal weights. All the mixings were vulcanised for the same time and at the same temperature, and vulcanisation coefficients of the standard and accelerated mixings determined. The excess of the vulcanisation coefficient over the standard was found to be highest in the case of *p*-phenylenediamine, which with one exception possessed the lowest dissociation constant of all the compounds examined. Benzidine with a dissociation constant of  $7.4 \times 10^{-13}$  gave an excess coefficient of 3.05, whereas methylaniline, the dissociation constant of which is  $2.55 \times 10^{-10}$ , gave an excess coefficient of only 0.612.

In a homologous series the activity of the various members is generally equivalent for gram-molecular proportions in the case of simple derivatives. Thus, for equal weights the higher members will be relatively less active than the lower members; dimethylamine dimethyldithiocarbamate is slightly more active than the corresponding diethylamine derivative.§ That this is not invariably the case is shown by the fact that for equal weights tetraethylthiourea disulphide is slightly more active than the corresponding tetramethyl derivative, especially in the absence of zinc oxide.|| Again, marked differences in activity are sometimes met with in the case of isomerides, for example, *p*-phenylenediamine is a much more effective accelerator than *m*-phenylenediamine. Of the thioureas obtained by the interaction of carbon disulphide

\* Kratz, Flower and Shapiro, *J. I. E. C.*, 1921, **13**, 129.

† Twiss and Brazier, *J. S. C. I.*, 1920, **39**, 131 T.

‡ *J. I. E. C.*, 1921, **13**, 67.

§ Schidrowitz, de Gouvea and Osborne, *I. R. J.*, 1922, **64**, 75.

|| Twiss, Brazier and Thomas, *J. S. C. I.*, 1922, **41**, 86 T.

with *o*-, *m*- and *p*-toluidine respectively, the di-*p*-tolylthiocarbamide is the most active, the ortho-derivative exhibiting the least activity.

In connection with the dithiocarbamates, it is interesting to note that, as Twiss, Brazier and Thomas (*loc. cit.*) have shown, those derived from primary amines are much less active than those from secondary amines, and the same is true of the corresponding thiouram disulphides.

The same authors have shown that dithiocarbamates from primary amines are not activated by zinc oxide to the same extent as are those from secondary amines, and if vulcanised to the same degree of distensibility the tensile strength of samples containing zinc oxide is lower than that obtained in its absence.

### EFFECT OF ACCELERATORS ON TENSILE PROPERTIES

If the saving of time in effecting vulcanisation were the sole advantage to be gained by the use of accelerators, they would on this account alone be of considerable interest to the manufacturer. Following their application on an industrial scale, it was soon evident that accelerated mixings gave vulcanisates of remarkably good tensile properties. This fact was first hinted at in 1918 by Spence,\* who stated that accelerators were "chosen to improve the physical qualities in addition to hastening the rate of vulcanisation."

Experiments described by Cranor† bore out this statement in a striking manner and showed that the high tensile properties were in many cases acquired at a comparatively low coefficient of vulcanisation.

A blank mixing of rubber (100), sulphur (6) and zinc oxide (1) was vulcanised for different periods at 144° C. to give a range of samples which were then tested for ageing properties. The vulcanisate attained after heating for 130 minutes and which possessed a vulcanisation coefficient of 2.85 gave the most satisfactory results. Addition of 0.5 per cent. of hexamethylene-tetramine gave a product after 50 minutes with a coefficient of 2.83, the tensile strength and toughness being much superior to those of the basic mixing.

With 0.5 per cent. of dimethylamine dimethyldithiocarbamate vulcanisation periods of three, four, and five minutes gave coefficients of 1.09, 1.21, and 1.45 respectively, in each case the tensile properties being of a very high order, as compared with the "blank" mixing. It was suggested by Cranor that with the reaction proceeding at an increased rate the amount of sulphur necessary to enter into combination to counteract the heat effect and so produce the characteristics of vulcanisation is less than the normal. It was shown that very low grade rubber which could not otherwise be vulcanised

\* I. R. W., 1918, 57, 281.

† I. R. J., 1919, 58, 1199.

satisfactorily gave quite good results when an accelerator was incorporated in the mixing.

Other workers have since corroborated these findings, Schidrowitz and Burnand \* having recorded a breaking load of approximately 2.7 kg. per sq. mm. in a sample cured with the aid of piperidine pentamethylenedithiocarbamate, the test being carried out after nine weeks' ageing at ordinary temperatures; the vulcanisation coefficient was not given, but from the figures quoted may be deduced as 1.8. Similarly, Twiss, Brazier and Thomas (*loc. cit.*) instanced the case of a sample containing tetraethylthiouram disulphide with a breaking load of over 2.8 kg. per sq. mm.

High tensile strengths obtained concurrently with low vulcanisation coefficients are generally met with only in mixings containing zinc oxide in addition to the accelerator. In the absence of zinc oxide both aldehyde ammonia and piperidine pentamethylenedithiocarbamate show normal coefficients with maximum tensile strength. The combination with sulphur is generally in direct proportion to the time of vulcanisation in absence of zinc oxide, but when zinc oxide is present the graph obtained on plotting combined sulphur against time is curvilinear.†

A rather curious phenomenon associated with the vulcanisation of mixings containing accelerators is the so-called "discontinuity" to which Twiss has directed attention.‡ In determining the distensibility as evidenced by the elongation produced by a given load, with increasing times of cure of mixings containing rubber, sulphur, hexamethylenetetramine and zinc oxide, it was noticed that the resistance to extension at first increased in the normal manner with increasing times of cure; in other words, the elongation produced by a standard load gradually diminished. On further heating this was followed by an increase in the elongation, after which the effect of heat was again reversed, the extension with increasing time of vulcanisation showing a gradual diminution. The curve obtained by plotting elongation at a load of 0.5 kg. per sq. mm. against time of heating was of the type shown in Fig. 12.

It should be remarked that this reversal of direction took place, not during the normal period of vulcanisation, but after the rubber had reached the stage at which it would be regarded as "correctly cured" from a manufacturing point of view.

The phenomenon differs from that of reversion, which is observed on prolonged vulcanisation of mixings containing low proportions of sulphur

\* *J. S. C. I.*, 1921, **40**, 272 T.

† Twiss, Brazier and Thomas, *J. S. C. I.*, 1922, **41**, 81 T.

‡ *J. S. C. I.*, 1921, **40**, 242 T; cf. also Twiss and Howson, *ibid.*, 1920, **39**, 287 T.

(see p. 122), and which is due to the heating being carried out in absence of sufficient free sulphur. In the cases quoted by Twiss, the reversal of properties takes place when there is still a considerable proportion of free sulphur present, and it is due to this free sulphur that the normal vulcanisation effect eventually supersedes the intermediate softening or disaggregation.

A reduction in the proportion of sulphur in the original mixing retards or prevents the recurrence of the normal vulcanisation effect when once softening has set in. Thus, in a mixing of rubber (95), hexamethylene tetramine (1), zinc oxide (1), containing 5 per cent. of sulphur, the distensibility at first decreases in the normal manner; this is followed by a rapid increase in distensibility, after which there is a scarcely perceptible recurrence

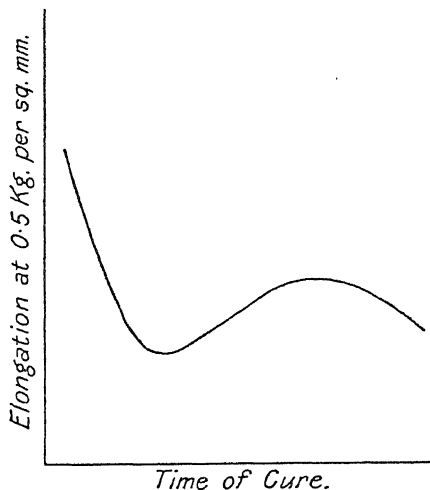


FIG. 12.

of the toughening effect. With only 3 per cent. of sulphur there is no recovery from the disaggregation, which from the time of its occurrence proceeds as in normal cases of reversion.

The softening does not take place in mixings containing only rubber, sulphur and accelerator, but is evident only when some undissolved solid matter, such as zinc oxide, china clay, or carbon black, is present. The effect is more marked in presence of small proportions of these ingredients and is obscured on adding further quantities. While the behaviour is most marked in the case of hexamethylenetetramine, other accelerators, such as *p*-toluidine, aniline, thiocarbanilide, and the dithiocarbamates, give rise to the effect in a lesser degree. In the case of the last named, the disaggregation is noticeable even when a considerable proportion of free sulphur is present.\* In

\* Twiss, Brazier and Thomas, *J. S. C. I.*, 1922, **41**, 82 T.

general, the reversion of the curve is accompanied by a lack of sharpness in the attainment of maximum tensile strength.

### ACCELERATION IN PRESENCE OF LOW PROPORTIONS OF SULPHUR

Although, for purposes of comparing the activity of accelerators, mixings containing as much as 10 per cent. of sulphur are frequently employed, it is generally realised that for technical purposes such high proportions of sulphur would be inadvisable, especially when the "ultra accelerators" are employed, as under these circumstances vulcanisation would proceed at ordinary temperatures and an over-cured rubber would result.

Schidrowitz and Burnand (*loc. cit.*) have examined the activity of piperidine pentamethylene dithiocarbamate in a mixing containing 2.5 per cent. of zinc oxide and only 2 per cent. of sulphur, which, without accelerator, is not sufficient to ensure satisfactory vulcanisation. Even with such a low proportion of sulphur, products were obtained with remarkably good tensile properties, although a minimum of approximately 0.5 per cent. of accelerator was necessary. With less than this amount the vulcanisates possessed inferior tensile properties. These results were confirmed later\* in a series of experiments in which the proportion of accelerator was kept constant (0.5 per cent.) and varying proportions of sulphur added. The full activity of the accelerator was evident only in presence of at least 2.5 per cent. of sulphur; with lower proportions the products gave poor tensile figures.

In a similar series of experiments Williams has shown† that in a basic mixing of rubber 100, zinc oxide 3, hexamethylenetetramine gives good results only when present to the extent of at least 0.5 per cent. in conjunction with at least 3 per cent. of sulphur; the best results were obtained with 1 per cent. hexamine and 3 per cent. sulphur. From this it will be seen that although in the presence of accelerators the percentage of sulphur may be reduced below that which is normally employed in their absence, the proportion of accelerator necessary to produce beneficial results may have to be increased over that which is effective with higher proportions of sulphur.

### ACCELERATION AT LOW TEMPERATURES

As has been stated in a previous chapter, vulcanisation proceeds, although comparatively slowly, at temperatures lower than those which are employed industrially. In the presence of active accelerators, however, vulcanisation

\* Schidrowitz and Bean, *J. S. C. I.*, 1922, **41**, 324 T.

† *I. R. W.*, 1922, **66**, 490.

may be effected at comparatively low temperatures within reasonable limits of time. In the case of a mixing which will vulcanise in, say, 300 hours at 90° C., the introduction of an accelerator with an acceleration factor of 300 for the percentage added would reduce the time of cure to one hour. Vulcanisation may indeed take place at ordinary atmospheric temperatures, as Cranor has shown. A mixing containing 6 per cent. sulphur, 1 per cent. zinc oxide, and 1 per cent. dimethylamine dimethyldithiocarbamate after storage for thirty-three days possessed a vulcanisation coefficient of 0.77 and a tensile strength of approximately 1.5 kg. per sq. mm.

If, instead of incorporating already prepared accelerators with the rubber-sulphur mixing, the accelerators are formed *in situ* by the interaction of other compounds, the activity is considerably enhanced. Thus Bruni \* has shown that if an aromatic amine such as aniline is incorporated with a rubber-sulphur mixing containing zinc oxide and the whole exposed to the vapour of carbon disulphide, vulcanisation will proceed at ordinary temperatures. Similarly if piperidine is added to a rubber cement containing zinc oxide and carbon disulphide, vulcanisation proceeds at ordinary temperatures much more rapidly than if the preformed dithiocarbamate were added.

This principle is capable of application in the case of many accelerators resulting from the interaction of two substances neither of which may possess marked activity when employed alone. Under these circumstances vulcanisation may be induced at comparatively low temperatures by incorporating one constituent with the rubber mixing and exposing this to an atmosphere charged with the vapour of the other. In this way coloured rubber goods may be produced by the use of dyestuffs which would not be permanent at ordinary vulcanising temperatures.

### EFFECT OF ACCELERATORS IN REDUCING VARIATION IN RUBBER

Shortly after the introduction of Plantation rubber complaints were made by manufacturers and others † that while the tensile properties were on the whole entirely satisfactory, the same could not be said of the time required for vulcanisation. It was found that different consignments of rubber did not exhibit the same rate of cure, with the result that when the standard conditions of time and temperature were applied in the works the manufactured articles were sometimes over-, sometimes under-cured. This behaviour was rarely met with when the various kinds of Brazilian Para rubber, or even

\* *J. S. C. I.*, 1921, 40, 520 A.; cf. also Bedford and Sebrell, *J. I. E. C.*, 1921, 13, 1034.

† Cf. Williams, *Rubber Industry*, 1914, p. 284; Schidrowitz, *ibid.*, p. 212.

the lower grades of wild rubber, were employed. The persistence of the complaints with regard to this "variability" led to a systematic study of the influence of different methods of preparation on the properties, more particularly the time of vulcanisation, of the rubber produced. The results of these investigations have been discussed in Chapter X, and from these it is evident that marked variations in the vulcanising capacity of the plantation rubber may arise from the mode of treatment at almost every stage in its preparation. As a consequence of these discoveries, efforts have been made to standardise the method of preparation so that a particular grade of rubber will always exhibit uniform vulcanising properties. While there is less heard of variability than was the case some years ago, it must be remembered that a proportion of the rubber in Malaya, roughly estimated as 20 per cent. of the whole, is produced in the form of unsmoked sheet on native small holdings, where the lack of a uniform procedure may be expected. Variations are, however, still encountered even in the higher grades of Plantation rubber.

It has frequently been stated that these variations in the rate of cure are not of considerable amount, since by the addition of accelerators the time of vulcanisation can be reduced so that the differences are eliminated or reduced to such an extent as to be negligible. It may be recalled that probably the first recorded case of variability\* was that of a consignment of rubber employed in a mixing containing litharge, the addition of which had evidently not had the effect of counteracting the differences in rate of cure. Stevens indeed has shown† that while in most cases the addition of litharge obscures variation in time of cure, in some cases, notably with rubber which has been attacked by mould, differences in the rate of cure are accentuated by the addition of litharge. It is suggested that this may arise from decomposition by the mould of some of the acetone soluble matter, which is essential for the development of acceleration by litharge.

The addition of organic accelerators might be expected to reduce variations in rate of cure, especially in cases where the proportion added is such that the time of vulcanisation is very considerably shortened. The question has been investigated by Martin and Davey,‡ who, in a series of preliminary experiments, vulcanised mixings containing rubber 90, sulphur 10, litharge 2, calcined magnesia 1, hexamethylenetetramine 1, different samples of rubber being employed. Under these conditions it was found that, judging by the elongation at a standard load and attainment of maximum tensile strength, variations found in "pure" rubber-sulphur mixing persisted even after

\* Thornton, *I. R. J.*, 1910, 40, 532 b.

† *Bull. R. G. A.*, 1922, 4, 520.

‡ *J. S. C. I.*, 1923, 42, 98 T.

addition of the accelerators specified. In some cases rubbers which cured relatively quickly in the absence of accelerators were comparatively slow-curing in the accelerated mixing. Judging by the vulcanisation coefficient after a definite time of cure, the variations noted were smaller in the case of the accelerated mixings.

Two of the rubbers exhibiting different rates of cure in a pure mixing were then taken and mixings made with organic accelerators only in the following proportions: rubber 90, sulphur 10, zinc oxide 5, accelerator 1. The accelerators used were thiocarbanilide, aldehyde-ammonia, *p*-phenylenediamine, *m*-phenylenediamine, "suparac" (piperidine pentamethylenedithiocarbamate on colloidal clay) and *p*-nitrosodimethylaniline. In each case the rubber which was the quicker curing in a pure mixing acquired the characteristics of vulcanisation more quickly than did the other. When incorporated in a mixing containing higher proportions of zinc oxide, 90 parts instead of 5 parts by weight per 100 of rubber, the differences in the rate of cure were practically obliterated in the mixings containing hexamine, *p*-phenylenediamine and "suparac," but the differences in the rate of cure still persisted in the mixing containing aldehyde-ammonia and to a less extent in that containing thiocarbanilide.

#### MODE OF ACTION OF ACCELERATORS

The action of accelerators in hastening the vulcanisation process is usually attributed to the conversion of the sulphur into an active form, probably through the intermediate formation of a compound capable of yielding "nascent" sulphur. As Peachey has shown (see p. 105), sulphur liberated *in situ* will effect vulcanisation almost instantaneously even at ordinary temperatures. It appears highly probable, therefore, that "accelerated" vulcanisation is due to sulphur being liberated from an unstable derivative resulting from a series of reactions in which the accelerator takes part. Most of the theories which have hitherto been propounded are based on an assumption of this nature. Owing to the widely different classes of compounds capable of functioning as accelerators, the mode of action may not be the same in all cases, and a comprehensive theory which will be universally applicable has not yet been propounded.

In the case of primary or secondary amines Ostromisslenski \* assumes the intermediate formation of thiozonides from which sulphur is subsequently liberated in an active form:

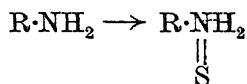


\* *J. S. C. I.*, 1916, 35, 370.



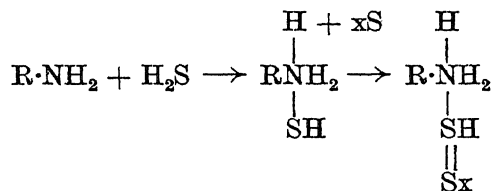
The manner in which the decomposition of the thiozonide occurs is not clearly explained, but it is somewhat vaguely described as undergoing decomposition with reproduction of the original amine or amine residue, which then reacts with a further quantity of sulphur to give once more the unstable thiozonide. It is difficult to see how the original amine can be formed from the hypothetical thiozonide, since two atoms of hydrogen have been removed in the primary reaction with sulphur. A more acceptable explanation would be that one of the three sulphur atoms is readily detachable as in the case of ordinary ozone, although even in this case the assumption would have to be made that the residual sulphur derivative would be capable of reuniting with a further atom of sulphur.

Kratz, Flower and Coolidge \* assume that addition of sulphur takes place at the nitrogen atom, which then becomes pentavalent :



Sulphur combined in this way is regarded as being loosely held, and consequently is taken up by the rubber, the amine being thus regenerated, after which the cycle is repeated.

A different explanation is offered by Scott and Bedford,† who assume vulcanisation to be effected by polysulphides analogous to ammonium polysulphide. The formation of the polysulphides is said to be as follows :



The hydrogen sulphide necessary for the formation of the amine hydro-sulphide arises from the known interaction of sulphur with the accessory substances present in the rubber. The polysulphide is regarded as the source from which the rubber derives the sulphur which brings about vulcanisation.

Compounds which react in this manner are designated "hydrogen sulphide polysulphide" accelerators, and to this class belong all basic organic accelerators which form polysulphides analogous to ammonium polysulphide.

A second class of compounds, termed "carbosphulphhydryl polysulphide" accelerators, comprises those which possess the group  $\equiv\text{C}\cdot\text{SH}$ , such as the thioureas, mercaptans, and dithiocarbamates. Thiouram disulphides are

\* *J. I. E. C.*, 1920, 12, 317.

† *Ibid.*, 1921, 13, 125.

regarded as derived from members of this group by the elimination of hydrogen as hydrogen sulphide. Compounds which belong to the "carbosulphhydryl" class form polysulphides directly with sulphur, whereas in the case of the "hydrogen sulphide" compounds the formation of hydrogen sulphide is necessary. From this it follows that carbosulphhydryl accelerators should function in rubber which has been deresinated, whereas hydrogen sulphide accelerators under these circumstances would be inactive owing to non-production of hydrogen sulphide; this, however, is true only if the acetone-insoluble nitrogenous constituent does not itself react with sulphur to yield hydrogen sulphide.

Inorganic accelerators are divided by Scott and Bedford into two classes : (a) primary accelerators, which include those compounds which are capable of forming polysulphides, as, for example, sodium hydrosulphide, calcium sulphide; and (b) secondary accelerators, which are assumed to function by removing hydrogen sulphide from organic polysulphides, and so facilitating the liberation of active sulphur, the original amine being regenerated.

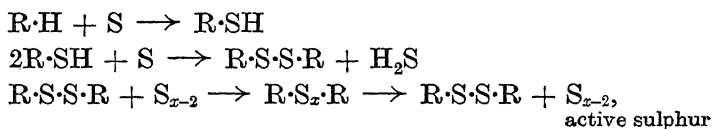
Some inorganic oxides and hydroxides may function both as primary and as secondary accelerators; thus, sodium and calcium hydroxides, acting as secondary accelerators, first form sulphides which are then capable of combining with sulphur to give polysulphides, thus acting as primary accelerators. Litharge and zinc oxide, on the other hand, are capable of acting solely as secondary accelerators, and do not form polysulphides under vulcanising conditions. This view was, however, modified later by the discovery \* that zinc persulphides were active vulcanising agents; moreover, experimental evidence was obtained which indicated that these persulphides were formed under the conditions of vulcanisation. Under these circumstances oxides, such as litharge and zinc oxide, would be regarded as "primary" accelerators. Similarly, when present together with dithiocarbamates, zinc salts would be formed which by addition of sulphur would yield polysulphides.

As examples of the hydrogen sulphide polysulphide accelerators may be cited aldehyde ammonia, the phenylene diamines, hexamethylenetetramine, and phenylated guanidines, of which the two last named also belong to the carbosulphhydryl class. Aldehyde ammonia yields ammonia when heated alone, and hydrogen sulphide when heated with sulphur, and is regarded solely as a hydrogen sulphide polysulphide accelerator. The action of *p*-phenylenediamine is similar, since, at vulcanising temperatures, reaction with sulphur takes place with formation of hydrogen sulphide and ammonia. Hexamethylenetetramine is said to function both by formation of hydrogen

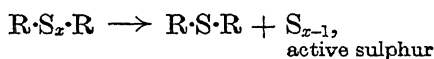
\* Bedford and Sebrell, *J. I. E. C.*, 1922, 14, 31.

sulphide on heating with sulphur and also by the production, among other compounds, of carbon disulphide and ammonia, which yield dithiocarbamates containing the group  $\equiv\text{C}\cdot\text{SH}$ . Phenylated guanidines by reaction with hydrogen sulphide give rise to thioureas and free amines, and so function both as "hydrogen sulphide" and "carbosulphhydryl" polysulphide accelerators.

Bedford and Sebrell conclude that all cases of acceleration by organic compounds (excepting nitroso-derivatives) may be summed up by the general scheme :



or more generally



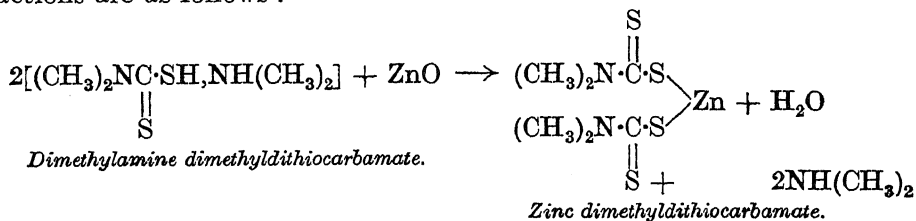
where R may be hydrogen, a metal, or a radical.

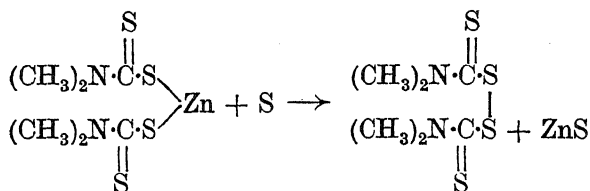
These authors regard the molecular form of the liberated sulphur as being the determining factor in effecting accelerated vulcanisation, and do not admit that the fact of sulphur being *in statu nascendi* is alone a sufficient explanation of its activity.

While the views of Bedford and his co-workers are based on the supposed intermediate formation of polysulphides, Bruni and Romani \* have formulated a theory based on the enhanced activity of certain accelerators in presence of zinc oxide. In the case of the dithiocarbamates and thiourea derivatives,

the activity is held to be a function of the grouping  $\begin{array}{c} \text{S} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{S} \end{array}$  or  $\begin{array}{c} \text{S}- \\ \diagup \\ \text{C} \\ \diagdown \\ \text{S}- \end{array}$  and not of the amino group.

In the presence of zinc oxide the zinc salt of the dithiocarbamate is first formed; this then reacts with sulphur to give the corresponding thiouram disulphide. In the specific case of dimethylamine dimethyldithiocarbamate the reactions are as follows :

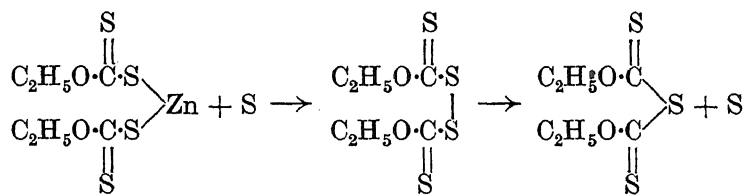




*Tetramethylthiouramdisulphide.*

Under the influence of heat this disulphide decomposes, giving the monosulphide and free sulphur which is then available for vulcanisation. As Romani \* had previously shown, thiouram disulphides are capable of effecting the vulcanisation of rubber without the addition of sulphur as such, although comparatively high proportions, of the order of 5 per cent. calculated on the rubber, must be added.†

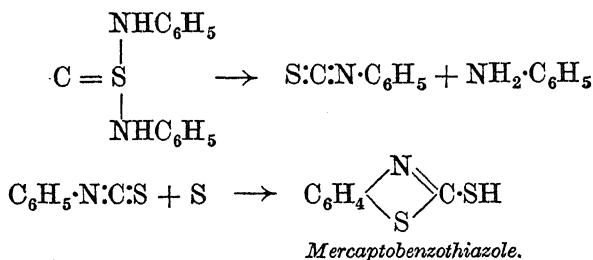
The action of zinc alkyl xanthates is assumed to be analogous to that of the dithiocarbamates, the corresponding disulphides, the dixanthogens, which are first formed, furnishing the necessary sulphur.



*Zinc ethylxanthate.*

*Diethyl dixanthogen.*

Thiourea derivatives are assumed to react in a somewhat analogous manner. The first step consists in the formation of phenyl mustard oil, which then reacts with free sulphur to form mercaptobenzothiazole.

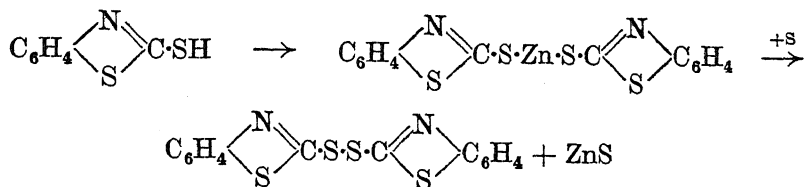


*Mercaptobenzothiazole.*

This is an acidic substance which alone is not capable of producing acceleration; in presence of zinc oxide the zinc salt is formed, and by a series of reactions similar to those outlined above, the corresponding disulphide is formed:

\* *J. S. C. I.*, 1921, **40**, 520 A.

† Cf. Twiss, Brazier and Thomas, *ibid.*, 1922, **41**, 86 T.



As in the case of the thiouram disulphide, vulcanisation is effected by the sulphur which is liberated when the disulphide passes into the monosulphide. According to the theory of Bruni and Romani the proportion of sulphur rendered active and made available for vulcanisation is equivalent to one atom for two  $>\text{C}=\text{S}$  groups, whether present in a dithiocarbamate, xanthate or thiourea derivative; concurrently, one molecular proportion of zinc sulphide should be formed. If it is assumed that the whole of the sulphur combined with the rubber is furnished by reactions such as those outlined, the production of a vulcanised rubber with a vulcanisation coefficient of 1.0 would necessitate, in the case of dimethylamine dimethyldithiocarbamate, the presence of approximately 10 per cent. of accelerator. It is known, however, that very small proportions of such a compound, for example, less than 0.5 per cent. in a 90 : 10 rubber-sulphur mixing containing zinc oxide, can cause vulcanisation to proceed in a few minutes at a temperature of  $140^\circ \text{C}$ . This could be explained by assuming that the monosulphide formed from the thiouram or other disulphide is capable of combining with the sulphur present to reform the disulphide, which then undergoes decomposition as before. Under such circumstances the presence of a small proportion of accelerator from which an unstable disulphide could be produced under the conditions of vulcanisation should be capable of furnishing a large proportion of sulphur through the monosulphide functioning as a sulphur carrier. Whether such a scheme is contemplated by Bruni and Romani is not clear from their exposition of the mechanism of the action of "ultra accelerators," but it is not definitely formulated, although their views have been interpreted in this way by Bedford.\* In this case the theory of Bruni and Romani closely resembles the polysulphide theory of Scott and Bedford, and differs essentially only in respect to the assumed sulphur carrier. Both theories afford a partial explanation of the action of zinc oxide in activating accelerators. According to Bruni and Romani, zinc oxide is necessary for the formation of a zinc salt which by reacting with sulphur gives rise to the thiouram or other disulphide. Scott and Bedford assume that the zinc oxide acts by giving rise to a zinc salt which by union of sulphur with the zinc is capable of forming polysulphides.

\* *J. I. E. C.*, 1922, 14, 857.

The fact that organic zinc salts are produced even at ordinary temperatures in the case of certain accelerators has been shown by Bedford and Sebrell,\* who found that a rubber cement containing zinc oxide and sulphur became clear on standing after the introduction of aniline or toluidine, together with carbon disulphide. This is attributed to the zinc oxide reacting to form a zinc salt soluble in benzene; in some instances crystals of the zinc salt were deposited in the cement. The need for an excess of zinc oxide over that necessary for the formation of the zinc salt is not, however, satisfactorily explained. It has been shown † that even when the previously prepared zinc dithiocarbamates or alkyl xanthates are added to a rubber-sulphur mixing, acceleration is produced only in presence of additional zinc oxide; similarly thiouram disulphides are activated by the addition of zinc oxide. Thus, the action of zinc oxide must extend beyond that indicated by the formation of the zinc salt of an acidic derivative of the accelerator. It has been suggested by Bedford and Grey,‡ and also by Whitby,§ that the function of the zinc oxide may be to neutralise acidic substances either arising from decomposition of the accelerator or present in the rubber resins.

An explanation of the mechanism of the action of nitroso-compounds, especially those, such as nitrosobenzene and nitrosophenol, which do not contain an amino group, is not yet forthcoming. Bruni and Romani (*loc. cit.*) suggest that a reaction may occur involving union of the nitroso-group with the double bond of the rubber hydrocarbon, in the same way that nitrosobenzene forms derivatives with unsaturated compounds, such as safrole and eugenol.|| An alternative explanation put forward by Bedford and Sebrell ¶ is that the nitroso-accelerators may function in a manner similar to that of litharge by promoting a reaction in which hydrogen sulphide is evolved, by effecting its oxidation and removal.

The supposition that acceleration is effected, as a rule, not by the compound introduced into the rubber mixing, but by a product formed by reaction with sulphur, has led to the suggestion to cause the accelerator to react with sulphur before incorporating it with the rubber.\*\* The advantage claimed for this procedure is that in certain cases the reaction with sulphur may take place only at temperatures higher than those ordinarily employed for vulcanisation, under which circumstances the substance added would not function as an accelerator. If, however, the substance is heated with sulphur at the

\* *J. I. E. C.*, 1921, 13, 1035.

† Twiss, Brazier and Thomas, *J. S. C. I.*, 1922, 41, 81 T.

‡ *I. R. J.*, 1922, 64, 604.

§ *J. S. C. I.*, 1923, 42, 370 R.

|| Angeli, Alessandri and Pegna, *J. C. S.*, 1910, 98, Abs. 1, 552.

¶ *J. I. E. C.*, 1921, 13, 1036.

\*\* Goodyear Rubber Company, E.P. 130857.

required temperature before being incorporated with the rubber, the reaction product will then effect acceleration.

### APPLICATION OF ACCELERATORS

Although the number of compounds capable of acting as accelerators is exceedingly large, only a few of these are extensively employed in works practice. The considerations which influence the manufacturer in the selection of suitable accelerators have been outlined by Rosenbaum \* and by L. E. Weber.† In the first place, it may be pointed out that the most suitable accelerators need not be those which are most active; in fact, the activity of certain accelerators, especially at comparatively low temperatures, is sometimes an objectionable feature, owing to the occurrence of premature vulcanisation. This may take place during the preliminary operations of compounding and milling, in which case the rubber mixing will be unsuitable for subsequent use. Such premature vulcanisation is usually referred to as "scorching," and, in order to avoid this happening, the rubber may be made up into two separate batches, one of which contains the accelerator and other compounding materials excepting the sulphur, which is incorporated with the second batch. The batches are worked separately until they are almost of the desired plasticity, when they are united, and in this case the subsequent working is of short duration. In the case of very active accelerators which are worked into large batches of rubber, the mixing may, however, retain sufficient heat for incipient vulcanisation to occur. Another objection to the use of active accelerators is that owing to the small amounts required in order to produce the desired effect, errors in weighing may occur, and, in order to overcome this difficulty, such accelerators are frequently sold diluted down with zinc oxide.

Another method which has been patented consists in forming the accelerator *in situ* on some substrate such as china clay ‡; for example, piperidine may be absorbed in china clay and the whole then exposed to the vapour of carbon disulphide, when the dithiocarbamate derivative will be formed, and the material as marketed will consist of approximately 1 part by weight of accelerator and 3 parts by weight of china clay. Prepared in this way, the incorporation into a rubber mixing is facilitated and risk of error in weighing is minimised.

As a general rule, a reduction in time of vulcanisation to a short period, such as five minutes, is not sought for on account of the difficulty of controlling

\* *I. R. J.*, 1922, 63, 225.

† *Ibid.*, 1922, 63, 793.

‡ Schidrowitz and Catalpo, Ltd., E.P. 170682.

the time of heating, an error of a few minutes producing a much more detrimental effect than a similar error in a longer time of cure.

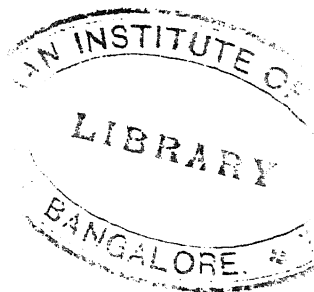
Another point which has to be considered in selecting an accelerator is its toxicity. *p*-Phenylene diamine, which gives very good results, is exceedingly poisonous, and is very little used at the present time. This has been reported on \* as probably the most poisonous accelerator hitherto proposed. Hexamethylenetetramine is liable to produce a rash, the occurrence of which may be avoided by washing the hands and arms in sodium bicarbonate solution.† Aniline, which at one time was largely used, but is only infrequently employed at present, also produces undesirable effects, and *p*-nitrosodimethylaniline has similarly been stated to cause skin troubles.‡

\* *J. I. E. C.*, 1918, 10, 865.

† Shepard and Krall, *I. R. W.*, 1919, 61, 75.

‡ Report of the Chief Inspector of Factories and Workshops, 1922.





## CHAPTER XIII

### METHODS OF MANUFACTURE

IN the foregoing chapters consideration has been given to the manner in which the properties of raw rubber may be markedly improved by the incorporation of suitable compounding ingredients and by submitting such compounded rubber to the process known as vulcanisation. It will be of interest to consider the general principles involved in the methods for reproducing these results on a manufacturing scale; a detailed description of works procedure is, however, not contemplated.

The first operation consists in the preparation of the raw rubber for use in the factory, which may be rendered necessary owing to the presence of undesirable foreign matter, such as sand, earth, wood splinters, etc., and also, in the case of Para rubber, on account of the 15 to 17 per cent. of moisture which is always retained by the biscuit.

It may appear strange that Plantation rubber, to the production of which so much care is devoted, should be contaminated with extraneous matter \* by treatment received in transit owing to the frequent opening of the cases at the wharves.†

It will be readily understood that a chip of wood if not removed may eventually be found in, say, the wall of a cycle tube and would soon lead to air leakage.

The rubber is therefore first softened and submitted to a washing process by passing through a series of mills similar to those described in dealing with crêpe rubber. As the rubber passes through the rollers, which are usually fluted, a stream of water from a perforated pipe is directed on to it, and in this way particles of foreign matter are washed out, the rubber itself being broken down into fragments which, however, cohere to form a continuous sheet with a crêpe-like surface (Plate 15a). After passing through these mills several times the crêpe is hung up to dry in a room kept at about 35° C., through which a stream of air is continually passing (Plate 15b). Recently there has been introduced a system of drying in which the rubber is exposed in a chamber,

\* B. D. Porritt, *I. R. J.*, 1922, 64, 421; "Symposium of Views of American Manufacturers," *I. R. W.*, 1922, 66, 602.

† H. P. Stevens, *I. R. J.*, 1922, 64, 825.

*e. g.* as in the Hunter Kiln,\* heated to a temperature of between 110° F. and 170° F., and the atmosphere within which is at a relative humidity of between 20 per cent. and 75 per cent. The air of a relative humidity of, say, 40 per cent., to take an intermediate value, and 70° C., will take up, to bring to the point of saturation, approximately 8 times as much water for a given volume of air as ordinary atmospheric air heated to 30° C. It is claimed on behalf of this apparatus that the presence of moisture in the air prevents the development of tackiness such as might result from drying in ordinary air at the same temperature. In this connection it may be recalled that Stevens has shown that vulcanised rubber deteriorates much less rapidly in moist than in dry air.† The employment of a moist atmosphere, therefore, admits of the rubber being dried at a comparatively high temperature, and therefore in a much shorter time than in an ordinary drying-room.

Another method of drying rubber is by means of the vacuum drier, a chamber from which the air can be exhausted, and which can be heated to a suitable temperature by means of steam or hot water.

### MILLING

The washed and dried rubber, in cases where this is necessary, or the rubber as received, is then submitted to the first operation incidental to the manufacture of rubber articles. This is known as grinding or milling, the object of which is to render the rubber plastic in order that the sulphur and other necessary ingredients may be incorporated.

This plasticising or "milling" is usually performed by passing the rubber between steel rollers slowly revolving in opposite directions at different speeds. (See Plate 16a.) Heat is generated in the process, and in order to prevent over-heating, the rollers are cooled by means of a stream of water passing continuously through a centrally bored cavity.

The rubber gradually becomes plastic and eventually forms a continuous sheet which adheres to one of the rollers; during the process the operative continually cuts away portions from the sides of the sheet and replaces these in another part of the roll, thereby ensuring the production of a homogeneous mass. The subsequent treatment of this milled or masticated rubber depends on the type of article to be produced and the method of vulcanisation to be employed.

### HOT VULCANISATION

Assuming that the vulcanising agent is to be sulphur, and that a heat process is to be adopted, the next operation is that of "mixing" or "compound-

\* E.P. 138915.

† See p. 127.

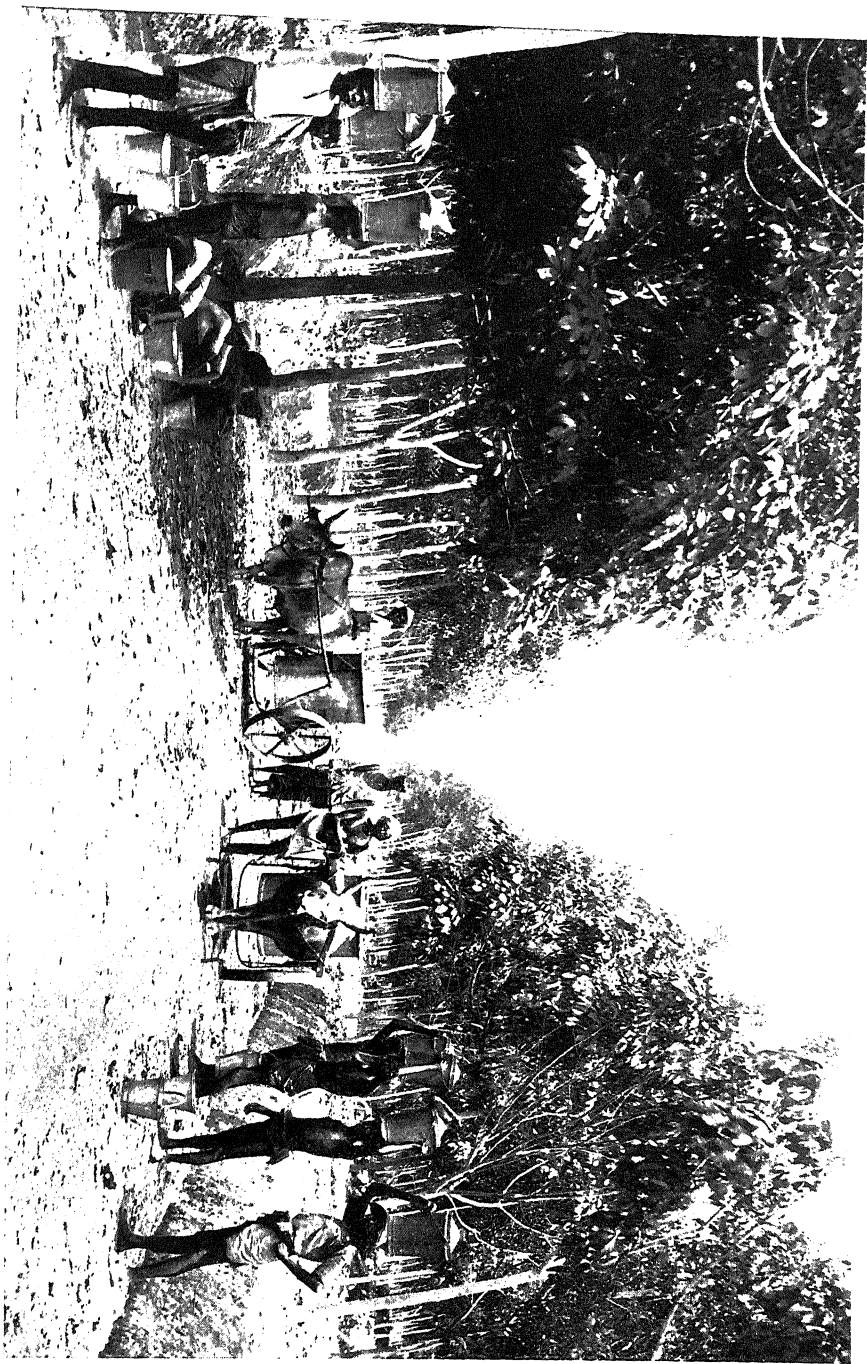


PLATE 6.—TRANSPORTING LATEX.



PLATE 15(A).—WASHING RUBBER.



PLATE 15(B).—RUBBER DRYING ROOM.

ing," in which the compounding ingredients, frequently referred to as "drugs," are incorporated with the plastic rubber. The mixing is performed on rolls similar to those used for the preliminary mastication, the sulphur and other adjuvants being gradually added, forming with the rubber a homogeneous mass. The mixing rolls are usually provided with hoods and connected to ducts through which air is drawn, thus effecting the removal of dust particles which might otherwise pass into the room to the detriment of the workers. In certain cases where lead compounds are introduced, special precautions, such as these, must be adopted in accordance with the requirements of the India Rubber Regulations, 1922; where such an installation does not exist, manufacturers may avail themselves of the already compounded mixtures of rubber and litharge which are now placed on the market.\* Such mixtures of rubber and litharge do not generate dust, and are therefore not regarded as lead compounds.

The plastic mixture of rubber, sulphur and other ingredients is now in a "tacky" or adhesive condition, and contains all the essentials for vulcanisation, which, however, will not take place until the whole is submitted to the required temperatures.

Thus, a complex article, such as a glove, may be constructed from several sections of rubber which in the tacky condition will weld together; when complete the whole is submitted to the heating process, when vulcanisation will take place, the tackiness will disappear, and the form taken up during vulcanisation will be retained permanently. This is the basic principle of rubber manufacture, the adhesive mixture of rubber, sulphur, etc., being capable of manipulation in a variety of ways until the vulcanisation process imparts to it the form in which it eventually appears on the market.

The operation succeeding that of milling will depend on the nature of the article to be made, and may consist in (a) making into a "dough" or solution, if a proofed cloth is required; (b) calendering to give a sheet of uniform thickness; (c) forcing through a die to give a tube or solid strip.

### PROOFED CLOTH

The proofing of cloth is usually accomplished by the operation known as "spreading," which consists in passing the fabric over a roller upon which rests a blunt knife known as a "doctor," in front of which is placed a quantity of rubber dough or solution. The position of the "doctor" knife is adjusted so that a thin coating of the dough is allowed to adhere to the cloth as it passes between the roller and the "doctor." The cloth is subsequently passed over a steam chest which causes evaporation of the solvent, so that after travelling

the length of the chest the coating of rubber is dry. The dough is made up by masticating the rubber together with the desired proportion of solvent, which may be either coal tar or shale naphtha. The rubber is first compounded with the necessary pigments, accelerators, and sulphur in cases where hot vulcanisation is to be employed, and is then passed to the dough mill, which usually consists of a trough provided with revolving blades. During the operation of spreading, the solvent which is evaporated is usually recovered, and numerous processes have been devised for effecting this.\* In order to obtain a coating of rubber of the required thickness it may be necessary to repeat the spreading process a number of times, and in some cases as many as twenty coats may be required. The cloth may be proofed on one side only or it may be proofed on both sides. Frequently the cloth is made up into what is known as "double texture," *i. e.* the fabric proofed with the dough on one side is "doubled" along with a second fabric, which adheres readily to the proofed surface owing to the characteristic adhesive nature of the unvulcanised rubber. If the cloth is to be proofed on one side only, the tacky coating of rubber is dusted with some material, such as French chalk or starch, which prevents it sticking to other surfaces. The material is usually vulcanised by winding round a drum and an outer covering of cloth wrapped tightly round. The drum is then exposed in an autoclave to steam at high pressure for the period necessary to effect vulcanisation. This may, for example, be four hours at a temperature of 140° C., or less in cases where accelerators are employed. In cases where the proofing is situated between two layers of fabric, as in the double texture material, or where the colour is required to be black, the vulcanisation may be effected by the "dry heat" process. In this case it is necessary to incorporate litharge with the mixing, as only by so doing is a satisfactory vulcanised article produced. Fabrics may be vulcanised by the "cold cure" process, in which case the dough does not contain sulphur. The proofed cloth may be vulcanised either by means of sulphur chloride in the form of solution, or in the form of vapour, or by the Peachey process. In the "cold cure" process the sulphur chloride is dissolved in a solvent such as naphtha or carbon tetrachloride, and the proofed fabric is passed through the sulphur chloride solution, effecting vulcanisation at the surface of the rubber film. Alternatively, the proofed fabric is suspended in a chamber into which is led the vapour of sulphur chloride. Vulcanisation proceeds rapidly and the bulk of the sulphur chloride is absorbed from the air in the chamber. In both cases it is necessary to expose the vulcanised material to an atmosphere of ammonia gas in order to neutralise any acid which may be formed from the sulphur chloride.

\* Wild, *I. R. J.*, 1923, 65, 313.

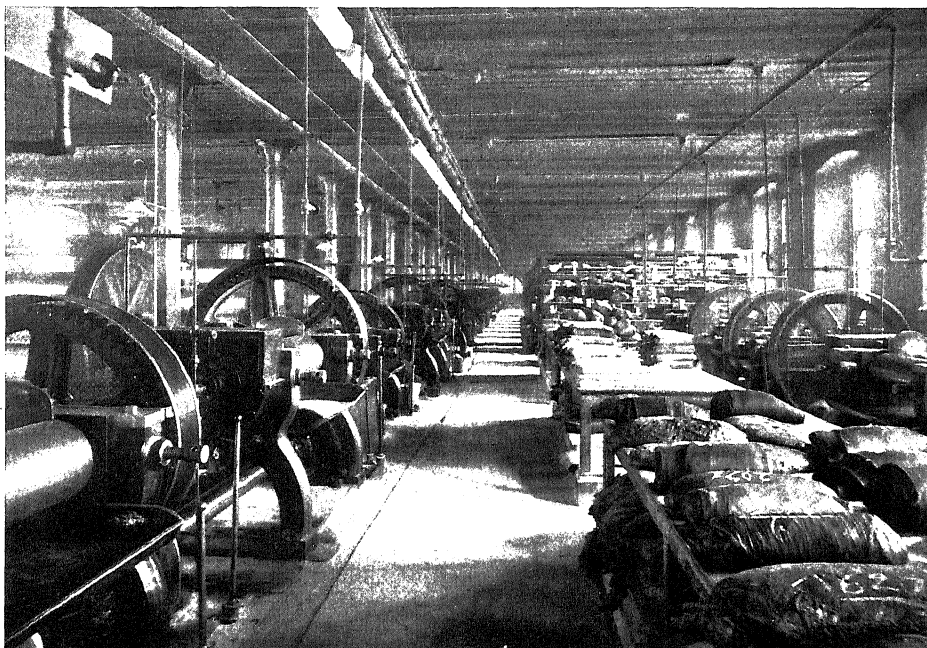


PLATE 16(A).—LINE OF MIXING MILLS, SHOWING BATCHES OF COMPOUNDED RUBBER.

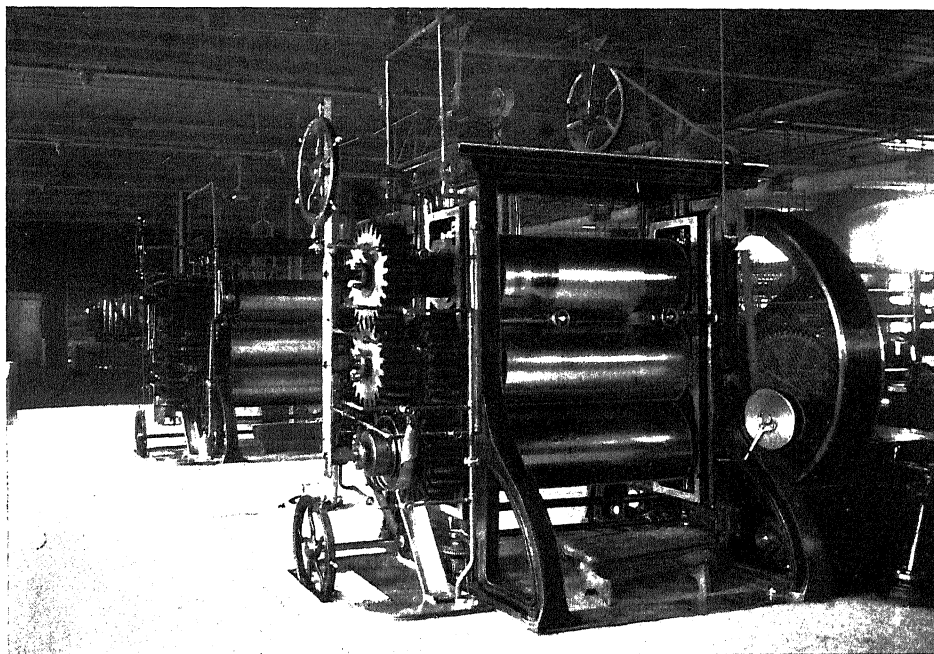


PLATE (16)B.—CALENDER, 3-BOWL.

## CALENDERING

The object of calendering is to produce sheets of uniform thickness which can be used for the building up of rubber articles. The rubber containing all the necessary vulcanising ingredients is first rendered plastic, and is then fed into the calender (see Plate 16b), which usually consists of three rollers or "bowls" situated vertically, one above the other. The upper and lower bowls revolve in the same direction, the central bowl revolving in the opposite direction. The softened rubber is fed in between the upper bowls and adheres to the central roller; then passes between this and the lower roller, through which a continuous roll of fabric is drawn at the same rate as the travel of the roller. The fabric is first dusted with some suitable material, such as French chalk or starch, in order to prevent the rubber sheet adhering too firmly, and in this way the fabric with the adherent rubber sheet can be rolled round a wooden core and is then ready for use. In some cases the calender bowl may be engraved with a suitable pattern, an impression of which is retained by the rubber.

## FORCING OR EXTRUDING

When the rubber article is required in continuous lengths having a definite cross-sectional area, as, for example, in the case of tubing, car tyre, etc., the plastic rubber is fed into a machine which consists essentially of a hollow cylinder provided with a centrally situated "worm" shaft which fits closely to the walls of the cylinder. The rotation of the shaft causes the rubber to travel forward to the front portion of the cylinder, which is provided with a die of the desired cross section through which the rubber is forced. The extruded rubber emerges in the form of a long strip which is carried forward by means of a travelling conveyor belt.

## MANUFACTURE OF RUBBER ARTICLES

The preliminaries to the manufacture of rubber consist in the above described processes, whereby the plastic mass of rubber, together with the necessary ingredients, is converted into a sheet of uniform thickness, a strip of definite outline, or fabric provided with a coating of the rubber. The subsequent operations will depend on the nature of the article to be produced.

## MOULDED GOODS

The production of moulded rubber articles followed closely on the discovery of vulcanisation, and in 1846 Hancock \* claimed "the making, forming or

\* E.P. 11135.



shaping articles from the combination of caoutchouc with other substances in or upon moulds, plates or forms during the process of vulcanising, whereby the form of such articles is rendered permanent."

The process consists essentially in placing the compounded rubber between the two halves of the mould and submitting the whole to a temperature at which vulcanisation will take place while the mould is being subjected to pressure, usually hydraulic, although in some cases a screw-press may be employed. In some cases the plates of the press are steam-heated and the heat is communicated to the mould when this is placed between them. In this way most small articles are produced. Alternatively, the pressure is applied by means of a ram situated within an autoclave which, when the articles are in position, may then be closed and steam admitted. This method is usually adopted for the manufacture of tyres. As a result of the heating vulcanisation takes place and the rubber preserves the sharp impression of the mould. Hollow-moulded goods are made from calendered sheet, and the internal pressure is usually obtained by inclusion of a definite quantity of ammonium carbonate, which dissociates at the vulcanising temperature.

While certain articles are capable of being moulded by means of a two-piece mould, in some cases the construction is more complicated and the mould may have to be constructed in three or four parts to give the desired effect. In the vulcanising of tyres, for example, besides providing for moulds to give the impression on the exterior of the tyre, a central core must be provided to act as a support; in some cases this is of metal, but latterly, especially in the construction of cord tyres, a rubber air bag has been adopted.

### OPEN HEAT VULCANISATION

Another method of vulcanising rubber by the hot process is that known as "open heat" cure, in which case the rubber is not enclosed between the surfaces of a mould, but is simply exposed under suitable conditions to a vulcanising temperature. In some instances the article is merely embedded in French chalk in a vessel which is then enclosed in an autoclave, and live steam admitted under pressure, say from 40 to 60 lbs. per square inch. In this way ordinary rubber tubing is made. It may, however, be necessary to support the rubber article on a form or mandrel in order that it may preserve its shape. A glove, for example, would be built up from calendered sheet on a form or last, and the whole embedded in chalk. Rubber hose, again, may be supported on a metal tube termed a mandrel and the exterior surface wrapped with cloth. The object of embedding in chalk or wrapping with cloth is to protect the surface from being marked with condensed steam.

In the examples quoted the heating is carried out in a vessel under a comparatively high pressure, but by choosing a suitable mixing vulcanisation can be induced by exposing the compounded rubber to a hot atmosphere at ordinary pressure. This is the method usually adopted for making black articles such as boots and shoes, in which case the rubber must be compounded with litharge, as only under such circumstances will vulcanisation take place satisfactorily.

The process is usually known as the "dry heat" method.

### SPONGE RUBBER

The production of sponge rubber was evolved as a result of the accidental formation of pores or blisters during vulcanisation. This observation led to the introduction of ammonium carbonate or other volatile compounds, or compounds capable of yielding a volatile product, with the object of producing a high degree of porosity in the finished rubber. Recently methods have been developed for making a cellular material by exposing compounded rubber to gases at high pressures. The rubber thus becomes saturated with the gas, and on releasing the pressure the gas is liberated to form minute pores.\* Similar rubber of this type has recently been found to be very effective as a heat insulator, and on this account has been recommended as a covering material for refrigerators. A modification of this process consists in the incorporation of carbon, which will aid in the absorption of gas. A further method of producing spongy rubber is that described by Schidrowitz and Goldsborough,† who employed rubber latex as the original material and incorporated in this the necessary inflating materials.

### DIPPED GOODS

Another method of producing rubber goods is by the process known as "dipping" in which the form is dipped into a solution of rubber in a suitable solvent. The form is then withdrawn and the rubber solution adheres. This is then allowed to dry to a thin film, and the operation of dipping repeated until the film is of the required thickness. The rubber is then vulcanised by dipping into a dilute solution of sulphur chloride. In this way articles such as surgical gloves, teats for feeding bottles, etc., are produced.

### VULCANITE

The black substance known as Vulcanite, Ebonite, or Hard Rubber is produced when high proportions of sulphur, *i. e.* for example, 50 per cent. calculated on the rubber, are employed. Vulcanisation is completed only

\* Pffeumer, E.P. 11624, 1911 ; Marshall, E.P. 162176, 1920.

† E.P. 111194, 1914.

after a considerable heating period. A large quantity of ebonite goods is made up by the moulding process, but on account of the duration of vulcanisation the outlay in moulds would be high. It is, therefore, usual to vulcanise the article only partially between the moulds and to complete the vulcanisation on a suitable form. Another method consists in inserting the rubber between two sheets of tinfoil, and the whole is then stamped from the master mould to the required shape, the tinfoil preserving the contour of the article during vulcanisation.

## CHAPTER XIV

### METHODS OF ANALYSIS

IN connection with the manufacture of rubber goods analyses may require to be carried out on (a) crude rubber; (b) compounding ingredients; and (c) vulcanised rubber.

#### CRUDE RUBBER

In the days before the advent of Plantation rubber, when the supplies of the manufacturer comprised a wide range of wild rubbers gathered and prepared by crude native methods, a rigid examination of each particular delivery was a necessity.

The rubber now obtainable on the open market is, however, of a remarkably standard composition, and it is rarely that an analysis is called for. Apart from the possible presence of mechanical impurities, such as wood, sand, etc., there is little likelihood of other extraneous matter having been added either accidentally or otherwise. The external appearance of the rubber is almost sufficient guarantee of its freedom or otherwise from adjuvants. In any case rubber is never bought or sold upon the basis of a specific chemical composition, or even of its possessing certain mechanical properties, but solely on its appearance. None the less a supply which could not rightly be said to conform with the characteristics of the particular grade would be regarded as just cause for complaint.

*Loss on Washing.*—The presence of an excessive proportion of mechanical impurities will be revealed by the loss in weight obtained on washing by the process already described. A weighed batch of the rubber, say 28 lbs., is treated in this manner and dried in the usual way, the loss in weight being thus ascertained. The loss will be due to moisture originally present, to mechanical impurities, and to any water soluble matter which may have been removed. Typical washing losses are as follows :

	Per cent.
Para Fine Hard . . . . .	16-18
Plantation Smoked Sheet . . . . .	1.0-1.3
Plantation Pale Crêpe . . . . .	0.5-1.0
Plantation Brown Crêpe . . . . .	4-6

The batch of rubber after washing and drying will serve as a representative sample for subsequent analyses excepting the moisture determination.

*Moisture.*—If the rubber is sufficiently clean to admit of its being used without previous washing, it will be necessary to determine the percentage of moisture present, as the use of a rubber containing a too high proportion (*i. e.* more than 0.5 per cent.) may lead to porosity in the vulcanised article. Both crêpe and sheet rubber take up moisture when exposed to the atmosphere, the percentage absorbed depending on the humidity. This has been clearly shown by van de Leur, working with laboratory samples,\* and by Whitby,† operating on large samples under tropical conditions. Crêpe rubber tends to take up water more readily than sheet rubber when exposed to a moist atmosphere, probably owing to the greater surface exposed, but sheet rubber retains more moisture under normal atmospheric conditions due to the presence of serum solids, which are hygroscopic. The moisture may be determined by drying at 100° C. in a water oven, and if the operation is not too prolonged there is little danger of error arising owing to oxidation of the rubber. In the case of very wet samples the drying is best carried out in a jacketed tube through which an inert gas such as hydrogen, nitrogen, or coal gas freed from carbon dioxide is passed.

*Aqueous Extract.*—Water-soluble material is not, as a rule, present to a considerable extent in normal Plantation grades, but in cases where a process of evaporation has been employed, as, for example, in the production of sprayed latex rubber (see p. 44), water-soluble material may constitute as much as 7 to 8 per cent. of the whole. Thus, if rubber prepared by the spraying process becomes a normal Plantation grade, the determination of water-soluble material will probably constitute a recognised analytical procedure.

*Resins.*—The resinous constituents of raw rubber are determined by extracting a finely shredded sample with hot acetone in a suitable apparatus of the continuous type, for preference one which does not necessitate the use of corks. The American Chemical Society ‡ advocate the employment of a form of Wiley's apparatus in which the extraction thimble and condenser are situated within a large flask § containing the boiling solvent. Another very convenient modification of the Wiley extractor is that devised by Schidrowitz,|| in which the flask containing the boiling solvent is provided with a mercury sealed cup into which is inserted a wide tube carrying the extraction thimble, which may be either straight or of the Knöfler type. The condenser is inserted

\* *Delft Comm.*, 2, 40.      † *J. S. C. I.*, 1918, 37, 278 T.

§ *J. S. C. I.*, 1893, 12, 548; *J. I. E. C.*, 1917, 9, 314.

|| Schidrowitz and Kaye, *J. S. C. I.*, 1907, 26, 127.

‡ *J. I. E. C.*, 1923, 15, 309.

at the top of the wide tube, and the vapours being condensed, the liquid drops on to the contents of the thimble and hence back to the flask. After extracting for five hours the residue obtained after evaporating off the acetone is dried to constancy at 90° C. The acetone extract is generally referred to as the "resin," but, as Spence and Kratz \* have shown, there is also present a nitrogenous substance; the nitrogen content calculated on the original rubber is usually of the order of 0.05 per cent.

In the case of "whole" rubber (*i. e.* evaporated latex) the acetone will extract a proportion of water-soluble material unless the sample has been previously washed with water.

*Protein.*—The nitrogenous constituent of rubber may be determined by a direct method (see p. 51), such as that of Spence and Kratz,† which consists in dissolving the rubber in a suitable solvent, adding trichloroacetic acid to reduce the viscosity of the solution, and filtering off the material remaining in suspension. The more usual procedure is to determine the percentage of nitrogen by the Kjeldahl method, and by means of a suitable factor to calculate the percentage of nitrogenous constituent. Howie,‡ employing Wilfarth's copper sulphate modification, has carried out experiments showing that it is not necessary to heat until the carbon formed at first is completely oxidised; at the end of three to four hours it was found that the conversion into ammonia was complete, although the liquid was still dark in colour. The factor for conversion of nitrogen to protein, 6.25, is usually adopted for expressing the results in terms of the nitrogenous constituent. According to Spence and Kratz (*loc. cit.*) a higher factor would probably be more correct, as in their opinion the nitrogen is present not as a simple protein but as a glucoprotein. The percentage of nitrogen present in raw Plantation and Para rubber is generally between 0.45 and 0.50 per cent.; of this approximately 10 per cent. is present in the form of a substance soluble in acetone.

*Ash.*—The sample is ignited in an open crucible and the ash weighed directly. The percentage of ash varies in different samples, Para rubber containing .03 to 0.5 per cent. and the better grades of Plantation rubber a similar proportion. Lower Plantation grades such as dark crêpe may yield as much as 1 per cent. owing to the presence of earth or sand. Sprayed latex rubber may yield even higher proportions (1.2 to 1.5 per cent.) of ash on ignition, and this is generally characterised by being strongly alkaline, as is that of Para rubber. The ash of Plantation rubber may contain, besides the naturally occurring inorganic matter, traces of reagents used either as anti-coagulants or for preventing darkening or mould formation in the crêpe or sheet.

\* *Koll. Zeit.*, 1914, 14, 268; cf. also Dekker, *Delft. Comm.*, 2, 55. † *Koll. Zeit.*, 1914, 14, 262.

‡ *J. S. C. I.*, 1918, 37, 85 T.

*Caoutchouc*.—The percentage of caoutchouc present in raw rubber is generally arrived at indirectly, *i. e.* by deducting from 100 per cent. the sum of the other constituents, estimated as described above. For technical purposes the figures thus obtained are sufficiently accurate and are indeed more reliable than those obtained by a direct method.

The simplest of the direct methods is that proposed by Fendler,\* which depends on the precipitation of the caoutchouc from a solution of the rubber by means of a liquid in which the other constituents are soluble: 2 grm. of the sample are dissolved in 100 c.c. petroleum ether, the solution filtered through glass wool, and the caoutchouc precipitated by means of absolute alcohol.

It is difficult, however, to remove the last traces of solvent, and frequently the precipitate carries down a proportion of the resinous material. Spence † recommended dissolving the rubber in benzene, allowing the insoluble constituents to settle and evaporating an aliquot portion in a stream of carbon dioxide.

Of the derivatives of caoutchouc the tetrabromide and the nitrosite are the only ones which are of a sufficiently definite composition to serve as the basis of an analytical procedure. A method for the determination of caoutchouc in raw rubber based on the formation of the tetrabromide was suggested by Budde.‡ This consists in first dissolving the sample in carbon tetrachloride, and after standing for twenty-four hours adding a solution of bromine, together with a small proportion of iodine in carbon tetrachloride. From the reaction mixture the tetrabromide is precipitated by adding alcohol, and after washing successively with a mixture of alcohol and carbon-tetrachloride, and then with pure alcohol, carbon disulphide is added in which the tetrabromide dissolves. It is then reprecipitated by adding light petroleum, and after filtering the precipitate is washed with alcohol until all traces of free bromine are removed.

The precipitate is then heated with a mixture containing excess of  $\frac{N}{5}$  silver nitrate and nitric acid (sp. gr. 1.40) so as to decompose the tetrabromide, with ultimate formation of silver bromide. The silver nitrate remaining unchanged is determined by the Volhard or other method, and the amount of silver nitrate used, and hence the bromine present as tetrabromides calculated. The proportion of caoutchouc corresponding to the bromine is assumed to be in accordance with the formula  $C_{10}H_{16}Br_4$ ; the percentage of caoutchouc is thus arrived at by multiplying the figure for bromine by the factor 0.425. The tetrabromide method has been the subject of much controversy,§ on the

\* *J. S. C. I.*, 1904, 23, 764.

† *Gummi Zeit.*, 1908, 22, 188.

‡ *Ibid.*, 1909, 24, 4.

§ See, for example, Harries and Rimpel, *ibid.*, 1909, 23, 1370; Hinrichsen and Kindscher, *Chem. Zeit.*, 1911, 35, 329; Spence, *ibid.*, 1909, 24, 212.

grounds that during bromination substitution occurs with consequent increase in the proportion of bromine entering into combination, a source of error which is to some extent compensated for by loss of HBr owing to instability of the tetrabromide. The interaction of bromine with the non-caoutchouc constituents is another possible source of error. Objection has been raised to the procedure adopted after obtaining the tetrabromide; Spence, Galletly and Scott\* having shown that in the treatment with nitric acid a loss of bromine occurs probably as an organic derivative due to traces of alcohol still remaining in the tetrabromide or to the presence of filter-paper.

In order to avoid such loss, fusion with sodium-potassium carbonate mixture has been suggested, and Utz† recommends heating the tetrabromide with a mixture of silver nitrate, sulphuric acid and potassium dichromate in a distilling flask and collecting the vapours expelled in absorption bulbs charged with a mixture of sodium sulphite and hydroxide. The absorption liquid is finally acidified with nitric acid and bromine determined as in Budde's

method after addition of excess  $\frac{N}{5}$  silver nitrate. The tetrabromide reaction has recently been investigated by Lewis and McAdams,‡ who have devised a purely volumetric process, based on that of McIlhiney,§ for determining the addition and substitution taking place on brominating unsaturated oils. The method consists in dissolving a known weight of the acetone-extracted rubber in pure carbon tetrachloride, filtering to remove the "insoluble" constituent, and adding a measured volume of bromine in carbon tetrachloride in sufficient quantity to provide an excess of 150 per cent. over that theoretically required. After the reaction has proceeded in the dark for two to four hours, the excess bromine is allowed to react with potassium iodide and the iodine liberated, titrated with sodium thiosulphate. Hydrogen bromide which may have been formed by substitution is then determined by adding potassium iodate and titrating the iodine liberated in this manner. Assuming that a true substitution has occurred, and that a proportion of bromine equal to that indicated by the second titration has entered the molecule, the original titration is corrected for the amount present as substituted bromine, and in this way it is claimed that accurate results may be obtained. Fisher, Gray and Merling,|| however, have examined the method, but have failed to get concordant results.

The nitrosite method for determining caoutchouc was first suggested by

\* *Gummi Zeit.*, 1911, 25, 801.

† *Ibid.*, 1912, 26, 968.

‡ *J. I. E. C.*, 1920, 12, 673.

§ *J. Amer. Chem. Soc.*, 1899, 21, 1084.

|| *J. I. E. C.*, 1921, 13, 1031.



Harries \* as a result of his study of the action of nitrogen trioxide on rubber (see p. 83). Of the three derivatives the nitrosite "C" formed by the action of the moist gas on a solution of rubber in wet benzene is the one having the most definite composition, this being in accordance with the empirical formula  $C_{10}H_{15}N_3O_7$ . Harries dissolves the rubber in benzene, and nitrous gases obtained by heating arsenic trioxide with nitric acid of sp. gr. 1.3 are led in until the solution becomes dark green. The precipitate formed is filtered off through a Gooch crucible, the precipitate washed and given a further treatment with the gases. After filtering again the nitrosite is washed with light petroleum, then with ether, and finally dried at 80° C. and weighed.

Alexander † recommended the employment of nitric acid of sp. gr. 1.4, a higher concentration than that advocated by Harries, and in his opinion the derivative obtained under these circumstances more closely corresponded with a "nitrosite" of the empirical formula  $C_9H_{12}N_2O_6$ . The formation of this compound was explained by assuming that during the reaction oxidation occurred with elimination of carbon dioxide. In this case the factor for conversion of the nitrosite to rubber would have to be modified to conform with the composition given by Alexander. The supposed loss of carbon dioxide during the preparation of the nitrosite is not accepted by Wesson,‡ who has evolved a method based on the combustion of the nitrosite and weighing of the carbon dioxide formed. In this way the assumption of a fixed composition for the nitrosite is avoided, since, in the event of there being no loss of carbon during the reaction with the nitrous gases, the nitrosite will contain all the original carbon of the rubber, and consequently the amount of carbon dioxide formed by combustion may be directly calculated to its equivalent of caoutchouc. Wesson and Knorr § have applied the principle of wet combustion for the final decomposition of the nitrosite, which is carried out by heating with a mixture of potassium dichromate and sulphuric acid.

Tuttle and Yurow || have investigated this method and have introduced a number of modifications in the procedure. The sample, after having been extracted with acetone, is dissolved in chloroform, and nitrous gases, from the interaction of arsenic trioxide and nitric acid of sp. gr. 1.30, are passed in until the green colour persists. After standing over-night the reaction mixture is filtered through a Gooch crucible and the filtrate evaporated to dryness. The residue, together with that on the filter, is dissolved in acetone, filtered, weighed, and, after settling, an aliquot portion

\* *Ber.*, 1902, **35**, 3256, 4429; 1903, **36**, 1937.

† *J. I. E. C.*, 1914, **6**, 459.

|| *I. R. W.*, 1917, **57**, 17; *U.S. Bureau of Standards Tech.*, Paper No. 145, 1919.

† *Ber.*, 1907, **40**, 1070.

§ *Ibid.*, 1917, **9**, 139.

of the liquid is evaporated to small bulk and transferred to a combustion boat. The last traces of organic solvent are removed by adding dilute ammonia and evaporating. The boat is placed in a combustion furnace and the products passed through a series of absorption tubes containing : (1), (2), (3) sulphuric acid and potassium dichromate, (4) powdered zinc, (5), (6) soda-lime and calcium chloride, (7) sulphuric acid and potassium dichromate, (8) dilute palladium chloride solution, the last to act as an indicator for carbon monoxide, the presence of which will point to incomplete oxidation. From the increase in the combined weight of tubes (5), (6), and (7) the weight of carbon dioxide formed, and hence the weight of caoutchouc, is ascertained. The direct methods outlined above are applicable to the analysis of vulcanised rubber articles, and reference will be made to them when dealing with this subject; for the analysis of raw rubber the indirect method is the more suitable.

### COMPOUNDING INGREDIENTS

The methods for the analysis of the various ingredients which are introduced into rubber mixings do not call for detailed commentary, since the ordinary analytical methods generally employed for pigments, oils, etc., are applicable. There are, however, certain points to be observed in examining raw materials for rubber manufacture. Thus impurities which are capable of producing a detrimental effect upon rubber must be rigidly excluded. For example, the presence of copper or manganese would lead to rapid perishing of the vulcanised rubber.

Acidity in the compounding ingredients should be guarded against, and a special watch should be kept on supplies which on account of their method of preparation are liable to contain acid. Lamp black prepared from an oil containing sulphur may be contaminated with sulphuric acid, and similarly sublimed sulphur usually possesses an acid reaction.

On the other hand, the presence of alkali in materials which should be neutral is equally to be avoided, since the introduction into a mixing may increase the rate of vulcanisation and an over-cured product be obtained if the normal factory procedure is followed.

In general, all pigments or filling materials should be free from grit, otherwise the particles may be apparent in the finished article. Microscopic examination will quickly reveal the presence of undesirably large particles.

Supplies which are liable to change on exposure to air must also be carefully controlled, otherwise imperfect vulcanisation may result. In the case of lime, which itself is an accelerator, exposure to air would result in the formation of calcium carbonate, which is without effect on the rate of vulcanisation.

In general, pigments should be chosen which will retain their colour under vulcanising conditions, and an indication of their stability may be obtained by heating with sulphur to  $140^{\circ}\text{C}.$ , under which conditions they should not undergo appreciable alteration. In particular, white pigments should be free from lead, otherwise during vulcanisation lead sulphide will be formed, which will lead to darkening in the finished product.

Lithopone should be free from natural barytes, the presence of which may be recognised by microscopic examination.\*

Antimony sulphide should be examined for the presence of free sulphur, calcium sulphate, and for higher sulphides which may undergo decomposition during vulcanisation and so furnish sulphur which will be available for vulcanisation. Luff and Porritt † recommend heating a weighed sample in a sealed tube to  $150^{\circ}\text{C}.$  in presence of a trace of ammonia in order to convert any "insoluble" sulphur which may be present into the soluble form, and simultaneously to liberate sulphur from higher sulphides such as the tetrasulphide  $\text{Sb}_2\text{S}_4$  ‡ or the pentasulphide.

The effect of varying particle size of fillers has been referred to previously (p. 152), and it has been shown to what extent the properties of the vulcanised rubber are dependent on this factor. Consequently it is important that the particle size should be ascertained in cases where it is of sufficiently small dimensions to affect the tensile properties.

One of the most satisfactory methods is that described by Green,§ which consists in preparing the pigment on a slide in such a way that a photo-micrograph may be taken at a known magnification. The negative is placed in a stereopticon and an image projected on to a screen divided into small squares to facilitate counting, the total magnification thus obtained being 20,000 to 25,000 diameters. The image of each particle is measured by means of a rule and the average particle size thus determined.

Vogt || has adopted a nephelometric method in which a known weight of pigment is dispersed in a measured volume of a suitable medium, *e. g.* glycerin, and the height of a column necessary to obscure a given source of light is determined. The underlying principle is that the smaller the particles, the greater will be the projected area interposed between the observer and the light, and, consequently, the less the height of the column of dispersed pigment necessary to bring about obscuration. The method is probably more suitable for determining the relative particle size of samples of the same pigment than

\* Stewart, *J. S. C. I.*, 1920, **39**, 188 T.

† *Ibid.*, 1921, **40**, 275 T.

‡ Kirchhof, *Zeit. anorg. Chem.*, 1920, **112**, 67; Short and Sharp, *J. S. C. I.*, 1922, **41**, 109 T.

§ *Jour. Franklin Inst.*, 1921, **192**, 637.

|| *I. R. W.*, 1922, **66**, 347.

for comparing samples of different composition and having dissimilar optical properties.\*

### VULCANISED RUBBER

It is clear, from what has been stated in the preceding chapters, that articles made from vulcanised rubber may contain, besides rubber and sulphur, pigments, filling materials, oils, bituminous substances and accelerators; if the sulphur chloride "cold cure" has been employed, halogen will also be present. The general scheme of analysis consists in determining the sulphur both free and in combination with rubber, organic material extractable with various solvents, inorganic constituents, and certain organic substances which are not extractable, such as glue, cellulose and free carbon.

For carrying out extractions the sample is usually cut up into fine shreds or cubes with scissors; alternatively, it may be ground in a suitable apparatus such as that described by Archbutt,† which consists of two grooved gun-metal rollers geared in the ratio 3 : 2, resembling a rubber mill. Wheatley and Porritt ‡ recommend the use of a rapidly rotating circular file, which gives satisfactory results in cases where the sample is of a comparatively rigid character.

*Acetone Extract.*—The comminuted sample, 1 to 2 gr., is placed in a filter paper thimble and extracted for eight hours with hot acetone in a continuous apparatus similar to that described under raw rubber. In this way there will be removed free sulphur, mineral and vegetable oils, paraffin wax, a proportion of bituminous substances present, and certain accelerators or their decomposition products. The acetone solution is evaporated in a weighed flask and the residue dried at 80° C. to constancy, the increase in weight giving the total acetone soluble material.

*Unsaponifiable Matter.*—This may be determined in a separate lot of the acetone extract by the usual methods applicable to oils.

*Paraffin Wax* in the unsaponifiable matter is usually determined by dissolving in hot alcohol and allowing to cool in ice, when the wax separates out; the whole is filtered and the wax dissolved off the filter by means of benzene or chloroform, the solution evaporated from a weighed flask, and the residue thus obtained weighed.

Other unsaponifiable matter may consist of part of the rubber resin, mineral oil or the acetone soluble portion of bitumen.

*Chloroform Extraction.*—The acetone-treated sample is submitted to extraction with chloroform, which removes a proportion of the tarry or bituminous substances. Extraction with pyridine was recommended by Weber,§ but

\* Feldenheimer, *Rubber Age*, 1922, 3, 8.

† *Analyst*, 1913, 38, 550.

‡ *J. S. C. I.*, 1915, 34, 587.

§ *The Chemistry of India Rubber*, 1902, Griffin.

Britland and Potts\* have shown that by so doing a proportion of the rubber may be "dissolved." On similar grounds the use of carbon disulphide, recommended by Caspari,† has been objected to by Porritt and Anderson.‡

It should be noted that bitumen as a rule contains matter soluble in acetone, the remainder being soluble in carbon disulphide; after vulcanisation, however, a part may become insoluble in both these solvents, so that even after carbon disulphide extraction the whole bitumen content may not be accounted for.§

*Alcoholic Potash Extraction.*—The sample, after the above treatment, is dried at 80° C. and then boiled with normal alcoholic potash for six hours; the liquor is filtered into a flask, the rubber washed with alcohol, which is added to the filtrate. The residue is finally washed two or three times with boiling water, which is added to the alcoholic alkali, and, when a volume of water equal to that of the alcohol has been added, the whole is acidified with hydrochloric acid to precipitate fatty acids. These are then extracted with three successive portions of ether, which are united, washed, and after evaporation the fatty acids are dried and weighed in the usual manner. By multiplying by  $\frac{100}{90}$  the weight of rubber substitutes made from fatty oils is arrived at.

The treatment with alcoholic potash will remove certain inorganic constituents, such as litharge or antimony sulphide, in addition to the rubber substitutes, and consequently the residual sample cannot be used for the determination of inorganic filling materials.

*Determination of Inorganic Filling Materials.*—In some cases where the inorganic materials used for incorporating with the rubber are stable towards heat, the determination may be carried out by the simple expedient of igniting in an open crucible and weighing the ash remaining. It is usual to carry out this operation by placing the crucible on a silica or asbestos plate provided with a central hole, and applying heat gradually so that the rubber does not catch fire, but is simply destructively distilled. The separate components of the ash may then be determined by the ordinary methods of quantitative analysis. This procedure cannot be followed in all cases, as, when volatile compounds are present, such as vermilion (mercuric sulphide) or antimony sulphide, only a portion or none at all may remain after ignition. Carbonates which undergo decomposition at comparatively low temperatures, such as basic magnesium carbonate, will also give fictitious values on heating in an open crucible. Other filling agents, such as talc, china clay, asbestos, lose water of combination and certain sulphides, for example, zinc sulphide, may be partially

\* *J. S. C. I.*, 1910, 29, 1142.

† *India-rubber Laboratory Practice*, Macmillan, 1914.

‡ *Rubber Industry*, 1914, p. 184.

§ Porritt and Anderson, *ibid.*, 1914, p. 185.

converted into oxides during incineration in presence of air. Reactions between constituents of the ash may also take place if oxygen is allowed access; thus, in a mixture containing calcium carbonate and chromium trioxide, calcium chromate will be formed on the exterior surface. Organic fillers, such as glue, carbon black and cellulose, will be burnt off and will not appear in the ash as determined by simple ignition. It is therefore desirable to perform a qualitative analysis first of all, and in doing so the colour of the sample will serve as a guide to its composition. Thus, a black mixing may contain free carbon or lead in the form of litharge, the presence of which leads to the formation of the black sulphide during vulcanisation. Similarly, a red sample may contain vermilion, antimony sulphide, iron oxide, an ochre, or an organic lake pigment.

In cases where the preliminary tests indicate the presence of substances which undergo changes during incineration a special method of analysis must be adopted.

It has been mentioned earlier that vulcanised rubber cannot be dissolved in the same way that unvulcanised rubber can, but when heated with certain high-boiling organic liquids at comparatively high temperatures the vulcanised material undergoes a process of degradation and a solution is thus obtained. Methods for separating the non-rubber constituents of mixings based on such a process of degradation have been devised, Weber,\* having proposed boiling the sample with nitrobenzene. The use of this solvent is open to many objections, chief of which is the fact that partial oxidation of the rubber is liable to occur. Many organic liquids have since been suggested, among them being anisol, phenetole, cumene and high-boiling petroleum. The acetone-extracted sample is heated in a flask under reflux until lumps of undegraded rubber are no longer discernible. The whole is then diluted with ether and the insoluble matter allowed to settle, or the separation may be hastened by centrifugalising. The clear liquid is poured off through a filter and the residue transferred to the filter by washing out with ether. The insoluble matter collected in this way may contain in addition to the inorganic constituents certain organic ingredients, such as glue, carbon black and cellulose.

This method may give satisfactory results in some cases, but difficulty is frequently encountered when finely divided substances such as zinc oxide, china clay, carbon black are present, as these remain in suspension for a considerable period, and, moreover, will readily pass through a filter.

Owing to the difficulties attending the determination of total filling materials by these methods it may be necessary to determine separately the components of the mixing.

\* *The Chemistry of India Rubber*, p. 247.

Antimony is best determined by a method similar to that outlined by Schmitz,\* in which the acetone-extracted rubber is decomposed by heating in a Kjeldahl flask with sulphuric acid containing potassium sulphate. The antimony may be determined in the acid liquor by a volumetric or gravimetric method. The acid is diluted and sodium sulphite added to reduce the antimony to the antimonous state, and excess of sulphur dioxide is removed by boiling; hydrochloric acid is then added and an aliquot portion titrated with standard permanganate solution. If iron is present it is necessary first to precipitate the antimony as sulphide, filter, and redissolve, or the antimony sulphide may be converted into the tetroxide by heating with concentrated nitric acid and weighed as such.

Mercury may be determined in a similar manner, the reaction product being diluted and mercury precipitated therefrom as sulphide. Frank and Birkner † treat a 0.5 grm. sample with 10 grms. ammonium persulphate and 10 c.c. of fuming nitric acid (sp. gr. 1.5), which is gently heated after the first reaction has moderated. The excess of nitric acid is subsequently removed by heating more strongly and the melt is taken up with 10 c.c. of hydrochloric acid (sp. gr. 1.12) and the solution diluted. The mercury or antimony may then be determined by the usual methods.

Where carbonates are present Goldberg ‡ recommends conducting the incineration of the sample in a porcelain boat enclosed in a glass tube, a current of nitrogen being passed during the heating; carbon dioxide lost on heating is collected in a soda-lime tube and the increase in weight added to that of the residue in the boat to give the total inorganic content.

In order to avoid errors due to oxidation during ignition, Goldberg's method may be employed or a similar one due to Schaeffer,§ which consists in heating in a current of carbon dioxide. In this way the residue will contain sulphides originally present as such, excepting vermilion, which will volatilise. Sulphide sulphur is determined in the residue by the usual methods. There is, however, a possibility of sulphides being formed during ignition if oxides are present, although the likelihood of this occurring will be diminished by working on an acetone-extracted sample.

*Glue.*—The finely comminuted sample previously extracted with acetone is warmed with water and tannic acid solution added to the aqueous extract, when a distinct cloudiness will indicate the presence of glue. Epstein and Lange || prefer first to digest the sample with cresol for sixteen hours at 120° C.,

\* *Gummi Zeit.*, 1911, 25, 1928.

† *Ibid.*, 1913, 37, 85.

‡ *Chem. Zeit.*, 1910, 34, 49.

§ *J. I. E. C.*, 1912, 4, 836.

|| *I. R. W.*, 1920, 63, 216.

whereby the rubber is brought into "solution." The whole is then diluted with petroleum ether and the glue and other insoluble constituents allowed to settle out. After decanting the supernatant liquid the residue is washed on to a Gooch filter with petroleum ether; it is there washed with hot benzene, after which it is allowed to dry and the residue boiled with water, and the filtered solution tested with tannic acid.

Samples containing glue will, as a rule, exhibit a marked loss in weight on drying at 100° C. due to the water present in the glue as used in the mixing. If bone glue has been employed the presence of a more than normal proportion of phosphate will be noted in the ash of the sample. The determination of glue is most satisfactorily accomplished by estimating the nitrogen present in the acetone-extracted sample by the Kjeldahl method. The nitrogen contained in the rubber must be subtracted from the total found; an average figure of 0.5 per cent. calculated on the rubber present may be taken for this purpose. It is therefore necessary to know approximately the proportion of rubber in the sample before the glue content can be arrived at. The figure obtained for the percentage of nitrogen, after correction, is multiplied by 6.5, to give the percentage of commercially dry glue (*i. e.* containing 15 per cent. water). In the determination the assumption is made that nitrogen is present in the acetone-extracted sample associated only with rubber and with glue. This may not always be the case, as when nitrogenous accelerators are used a proportion may be converted into acetone-insoluble substances during vulcanisation. At best, therefore, the method is capable of yielding only approximate values for the glue present.

*Carbon Black*, in its various forms, may be determined by destroying the rubber portion with nitric acid, which leaves the free carbon unattacked. In the method described by Smith and Epstein \* a 1 gram sample is extracted first with acetone, then with chloroform, after which it is dried and transferred to a beaker containing a few c.c. of concentrated nitric acid (sp. gr. 1.4), and the whole heated on the steam bath for an hour. The liquid is then poured through an asbestos pad in a Gooch crucible and the residue washed with nitric acid. The residue in the crucible is washed alternately with acetone and benzol until the filtrate is colourless. Lead, if present, is removed from the residue by washing with ammonium acetate, and metal oxides dissolved out with 5 per cent. hydrochloric acid. The crucible is dried in an air bath at 150° C., and at this stage contains carbon together with inert inorganic substances which have resisted the previous treatment. The crucible and contents are weighed, the carbon burnt off and the loss in weight determined;

\* *J. I. E. C.*, 1919, 11, 33.



this corresponds to the weight of carbon originally present. The authors find that the average figure for carbon found in this way is 105 per cent. of that actually present, and advise that the value obtained should therefore be multiplied by the factor  $\frac{100}{105}$ .

*Sulphide Sulphur.*—The most satisfactory method for determining sulphur present as metallic sulphide is that devised by Stevens,\* which depends upon the interaction of the sulphide with hydrochloric acid to give hydrogen sulphide, which is collected and estimated; the action of the acid is facilitated by allowing the sample to swell in ether. The decomposition is carried out in a flask fitted with a stopper, through which passes an inlet tube leading to the bottom of the flask and an outlet tube for the escaping gases. Pure concentrated hydrochloric acid (10–20 c.c.) is poured into the flask and covered with a layer of ether (20–30 c.c.), the air being then displaced by means of a stream of carbon dioxide or nitrogen. The outlet tube is connected with a series of two absorption flasks containing lead acetate solution, and the weighed comminuted sample is then dropped into the ether hydrochloric acid mixture and the reaction allowed to proceed at ordinary temperatures for fifteen to thirty minutes, a slow stream of gas being continually passed through the apparatus. The ether causes the rubber to swell, and the acid thus penetrates to the interior of the sample, causing liberation of hydrogen sulphide, which is carried to the absorption flasks, where lead sulphide is precipitated. The flask is finally immersed in warm water and the ether driven off and collected in the absorption flasks. The contents of the flasks are united and ether evaporated and acetic acid added to dissolve lead carbonate; the lead sulphide is then collected on a filter and washed with water. The filter paper, together with the lead sulphide, is then transferred to a stoppered bottle, standard iodine added and the whole shaken at intervals for a period of fifteen minutes. The excess iodine is then titrated with thio-sulphate, and from the amount used the lead sulphide formed, and from this the sulphide sulphur originally present may be calculated. While this method is applicable only to such sulphides as are decomposed by hydrochloric acid, these are the ones usually met with in rubber mixings; in case vermilion is present the proportion is arrived at from the determination of mercury.

*Carbon Dioxide* is determined by decomposing the ground sample with dilute hydrochloric acid and expelling the liberated gas by means of a current of purified air or nitrogen; copper sulphate should be added to the contents of the reaction flask in order to retain hydrogen sulphide. The issuing gas is

\* *Analyst*, 1915, 40, 275.

passed through a calcium chloride tube and carbon dioxide absorbed in caustic potash solution or soda lime. Pearson \* recommends heating the sample with glacial acetic acid, which causes complete penetration of the sample. The apparatus consists of a flask provided with a short reflux condenser, which is connected with a U-tube containing solid lead acetate; this is in turn connected with a second U-tube containing in one limb sodium acetate and in the other calcium chloride. The absorption is carried out in a soda-lime tube connected with a calcium chloride tube, both of which are weighed before and after the experiment; air is passed through the whole apparatus during the operation.

*Cellulose* may be present in conjunction with rubber either in the form of a continuous cord or fabric, as, for example, in tyre casings or in proofed textiles, or it may occur ground up with the rubber to form a more or less homogenous mass. Fabric occurring as such may be determined by Porritt's method,† in which the sample is first swollen in carbon disulphide and then heated with high-boiling petroleum in much the same manner as described on p. 217. In this way the rubber proofing is removed, leaving the fabric free from rubber but retaining a proportion of the inorganic fillers which become enmeshed between the threads. The sample is washed with ether, dried, and then boiled with sodium carbonate, followed by a similar treatment with dilute acetic acid, to remove inorganic materials which are not stable to heat. The fabric is finally washed with water, dried at 100° C. and weighed. The cellulose is then burnt off and the inorganic residue weighed, the loss being taken as the weight of moisture-free cellulose originally present. The result is calculated to air-dry cellulose by adding 8.5 per cent. of the figure thus obtained.

The method is applicable in cases where the compounding ingredients do not include carbon black or china clay. These would not be removed by the treatment recommended, and both the carbon lost on ignition and the water of combination expelled from the china clay would count as cellulose. In the event of china clay being present the cellulose would probably be determined by combustion, as suggested by Porritt.

In mixings where carbon black is present or where the cellulose in the form of waste is ground up with the rubber, the method of Epstein and Moore ‡ may be found more suitable. The sample is heated in a flask with cresol for four hours at 165° C., after which the whole is diluted with petroleum ether and filtered through a Gooch crucible. After washing first with hot benzene and then with acetone, the residue in the flask is transferred by means of hot 10 per cent. hydrochloric acid to the Gooch crucible and the washing with

\* *Analyst*, 1920, **45**, 405.

† *J. S. C. I.*, 1919, **38**, 50 T.

‡ *I. R. J.*, 1920, **56**, 559.

hydrochloric acid repeated several times. The residue on the filter is washed free from chloride with hot water and then with acetone until the filtrate is colourless; then treated with a mixture of carbon disulphide and acetone, washed with alcohol, dried at 105° C. and weighed. The cellulose in the residue is acetylated by heating on the steam bath with 15 c.c. acetic anhydride and 5 c.c. concentrated sulphuric acid for one hour. The whole is then filtered, washed with acetic acid, dried at 150° C. and the loss in weight reckoned as cellulose.

*Rubber.*—It has already been stated in dealing with raw rubber that a sufficiently accurate indication of the proportion of caoutchouc hydrocarbon present is obtained by determining the other constituents and regarding the rest as caoutchouc. The same may be said with regard to vulcanised rubber, although in mixings where constituents such as glue, bitumen, and cellulose are present, the results obtained by a direct method may be more nearly in accordance with the actual composition than those obtained by the difference method. The formation of caoutchouc tetrabromide, which has been taken as the basis of a quantitative method for the analysis of raw rubber, has also been applied to the examination of the vulcanised material. In the modification of Budde's method suggested by Axelrod \* a 1 gr. sample is heated for about two hours with 100 c.c. of petroleum (b. pt. up to 300° C.) in a flask under reflux. In this way the rubber undergoes degradation forming a "solution," 10 c.c. of which are removed and treated with Budde's brominating agent (see p. 210). After standing three to four hours, 100–150 c.c. absolute alcohol are added, the precipitate allowed to settle, then transferred to a filter and washed with a mixture of equal volumes of alcohol and carbon tetrachloride, finally with alcohol, and dried at 60° C. and weighed. The precipitate is incinerated and the residue weighed, the loss in weight being reckoned as caoutchouc tetrabromide. Theoretically the factor for converting the weight of tetrabromide to caoutchouc hydrocarbon is 0.298, but from a series of determinations Axelrod concluded that a factor of 0.314 gave results more nearly in accordance with the theoretical value for the technically pure rubber (*i. e.* containing the usual accessory substances). It was noticed that in all cases the precipitated tetrabromide contained the whole of the combined sulphur, which would vary for different mixings, and on this account an adjustment of the factor would be necessary. This was pointed out by Hübener,† who recommended treating the acetone-extracted sample (0.2 gr.) directly with a mixture of 5 to 10 c.c. bromine and 100 c.c. water in a flask heated gently on a sand bath until the reaction is complete. The excess of bromine is then driven off by heating more strongly and the reaction

\* *Gummi Zeit.*, 1907, 21, 1229.

† *Chem. Zeit.*, 1909, 33, 648, 662.

product filtered, washed with hot water, and then transferred to a flask containing excess of standard silver nitrate, together with 20 c.c. concentrated nitric acid, and the estimation proceeded with as described under raw rubber, the excess of silver being determined by titration. The method has been criticised by various workers,\* whose experiments, carried out with a comprehensive range of mixings, indicate that reliable results cannot be obtained chiefly on account of the difficulty of securing satisfactory bromination.

The nitrosite method, which has already been described (see p. 212), has also been applied to the examination of vulcanised rubber and is carried out in a manner similar to that employed in the case of raw rubber, excepting that the sample is allowed to swell in a suitable solvent before passing in the nitrous gases. According to Tuttle,† Wesson's nitrosite method, as modified by Tuttle and Yurow, is the only accurate direct method for the determination of rubber.

Of the two methods, the one based on the formation of the tetrabromide is simple to operate, and although it may not yield extremely accurate results, these may serve as a check on the figures obtained by a difference method. The nitrosite method, on the other hand, while giving more reliable figures, takes some considerable time and involves the use of a complicated apparatus.

A third method for the determination of the rubber hydrocarbon is that recommended by the U.S. Joint Rubber Insulation Committee‡ but it is not applicable to mixings containing ingredients such as free carbon, bitumen, or vermilion. Briefly, the method depends on dissolving from the rubber by means of hydrochloric acid all the inorganic constituents removable in this manner. Any undissolved residue contains only those substances which will not undergo change on heating, and therefore if the treated rubber is dried, weighed, and then incinerated, the loss in weight will be due entirely to rubber; it is necessary as a preliminary to extract the sample first with acetone, then with alcoholic potash, and finally with chloroform, before carrying out the hydrochloric acid treatment.

*Free Sulphur* is determined in the acetone extract by adding fuming nitric acid together with two or three drops of bromine and, after covering the flask with a watch-glass, warming on a steam bath for five hours. One gram. of sodium chloride is then added and the nitric acid allowed to evaporate by removing the watch-glass, the last traces being expelled by adding hydrochloric acid and evaporating once more. The sulphuric acid formed by

\* Hinricksen and Kindscher, *Chem. Zeit.*, 1912, **36**, 217, 230; Becker, *Gummi Zeit.*, 1912, **26**, 1503; Esch, *Chem. Zeit.*, 1911, **35**, 971.

† *The Analysis of Rubber*, American Chemical Society, Monograph Series, p. 79.

‡ *J. I. E. C.*, 1917, **9**, 310.

oxidation is then precipitated by adding barium chloride and the estimation proceeded with in the usual manner.

Pearson \* recommends the use of fuming nitric acid for carrying out the oxidation, which is completed by the addition of successive small quantities of potassium permanganate. The reaction mixture is evaporated to dryness and treated with hydrochloric acid, evaporated once more, and then taken up with hydrochloric acid and the sulphate precipitated with barium chloride.

In the method recommended by the American Chemical Society † bromine water alone is employed as oxidising agent, 50 c.c. of water and 2–3 c.c. of bromine being added to the acetone extract and the whole first heated cautiously for  $\frac{1}{2}$  hour, after which it is heated directly on a steam bath until the solution is colourless; after filtering and diluting to 175 c.c. with distilled water the sulphuric acid is precipitated by adding barium chloride.

*Total Sulphur.*—The total sulphur content of a sample may sometimes require to be known, but as a general rule this is of less importance than a knowledge of the proportion of sulphur present in combination with rubber, *i. e.* of the coefficient of vulcanisation. Several methods for the determination of total sulphur have been suggested, but for general purposes the Carius method is by far the most reliable. The only disadvantage attending the use of this method is that there is some uncertainty as to the result if sparingly soluble sulphates, such as lead sulphate, are present; barium sulphate will remain insoluble and the sulphur present will not be included in the result. The presence of barium carbonate will also lead to a fictitious value being obtained, since combination with the sulphuric acid will take place with formation of barium sulphate, which will be retained on filtering the reaction product. If then the total sulphur is required, a process involving fusion must be adopted in cases where the mixing contains ingredients of the type referred to.

The method originally proposed by Henriques ‡ has been generally favoured, slight alterations in the procedure having been suggested by several workers.§

In the modification recently adopted by the Committee of the American Chemical Society || a sample weighing 0.5 gr. is placed in a 75 c.c. porcelain crucible and 15 c.c. of a mixture of nitric acid and bromine added. The crucible is covered with a watch-glass, and allowed to stand for one hour in the cold, then heated for one hour, the cover removed and rinsed with water. The

\* *Analyst*, 1920, **45**, 405.

† *Zeit. Angew. Chem.*, 1899, **34**, 802.

§ Wagner, *Gummi Zeit.*, 1907, **21**, 657; Hubener, *ibid.*, 1909, **24**, 213; Waters and Tuttle, *J. I. E. C.*, 1911, **3**, 734.

|| *Ibid.*, 1923, **15**, 309.

† *J. I. E. C.*, 1923, **15**, 308.

contents of the crucible are evaporated to dryness,\* 3 c.c. nitric acid added, the crucible re-covered and the whole warmed for a short time on the steam bath. After cooling 5 gr. of sodium carbonate are added in small portions in such a way that the salt falls down the side of the crucible and does not drop directly into the acid. The watch-glass is rinsed with hot water and the mixture stirred thoroughly with a glass rod, being spread round the sides of the crucible to facilitate drying, which is conducted on a steam bath. The dried mixture is fused and the reaction controlled by the aid of the stirring rod; the melt is allowed to cool and the crucible placed in a 400 c.c. beaker, and sufficient distilled water added to cover the crucible, and the whole allowed to digest on the steam bath for two hours. After filtering into a covered 400 c.c. beaker containing 5 c.c. of concentrated hydrochloric acid the residue is washed with hot water, and the filtrate completely acidified. After warming on a steam bath, barium chloride is added to precipitate sulphate and the sulphur determined in the usual manner.

Methods have been described which do not involve a preliminary treatment with acid, as, for example, in those of Kaye and Sharp,† in which the sample is simply fused with a mixture of zinc oxide and potassium nitrate, and of Alexander,‡ who employs the well-known sodium peroxide fusion.

The chief objection to a procedure of this nature is that the particles of rubber cannot be intimately mixed with the fusion mixture, and incomplete oxidation results. Mixings which can be rasped to a comparatively fine state of division may be treated in this way, especially if the reaction is carried out in a Parr "sulphur bomb."§

### RUBBER-COMBINED SULPHUR

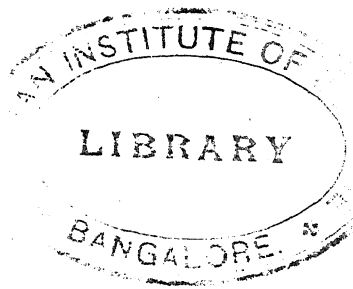
A knowledge of the proportion of sulphur in combination with rubber is necessary in order to arrive at the coefficient of vulcanisation. In mixings which contain only rubber and sulphur, or in those which do not contain sulphides, sulphates, or compounds which may give rise to these during vulcanisation, the determination of rubber-combined sulphur is a comparatively simple procedure. The sample is first extracted with acetone, and then, if fatty oil substitutes are present, with alcoholic potash, and the sulphur determined in the residue, preferably by the Carius method. The coefficient of vulcanisation ( $c$ ) is given by the equation  $c = \frac{100 S}{r}$  where  $S$  = percentage

\* It is best to add 0.2 to 0.3 gm. potassium nitrate before evaporation, otherwise, especially in mixings free from oxides or carbonates, there is a danger of charring taking place, the free sulphuric acid being reduced to sulphur dioxide by the organic compounds present.

† *I. R. J.*, 1912, **44**, 1189. ‡ *Gummi Zeit.*, 1904, **18**, 729. § *J. I. E. C.*, 1919, **11**, 230.

of sulphur combined with rubber in the sample of  $r$  = percentage of rubber. The rubber is arrived at by the difference method, after a complete analysis of all other constituents, and is generally expressed as technically pure rubber, *i.e.* rubber containing the naturally occurring resins, proteins, etc., and not as chemically pure caoutchouc hydrocarbon. In more complicated mixings, where such a procedure is inadmissible, it is best to eliminate as many as possible of the sulphur-containing substances before determining the sulphur combined with rubber. Thus, where zinc or lead sulphide is present the combined sulphur is determined on the residue left after the estimation of sulphide sulphur. This may still contain lead sulphate, and in this case the analysis must be carried out on a portion of the residue, the sulphate being determined on another portion after ignition. Barium sulphate, if present, will be retained on filtration of the acid liquor resulting from the Carius oxidation, and the sulphur present will not affect the estimation.

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